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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.

BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR
Division of Chemical Sciences

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NEW VARIANT OF THE DUMAS METHOD OF DETERMINING NITROGEN

V. A. Klimova and I. F. Dubinina

In the determination of nitrogen by the Dumas method it is essential to bring about the quantitative oxidation of the compound and at the same time obtain all the nitrogen in the form of elementary nitrogen. This is attained by the use of incandescent copper oxide as oxidant and incandescent copper as reducing agent for oxides of nitrogen. In this method both reduced copper and copper oxide are used in great excess. We consider that the use of such an excess of oxidizing and reducing agents is necessary only because the method of combustion is not satisfactory: the combustion is carried out by slow evaporation of the substance into the oxidation and reduction zones, and incompletely burnt fragments of the compound or unreduced oxides of nitrogen may be carried away in the convection of the hot gases through the filling of the tube. Also, products of the incomplete oxidation of the substance may condense in a thick layer in the still cold part of the filling and, in some cases, react chemically with the filling, e.g., in the analysis of nitriles, in which cuprous cyanide may be formed and may not yield the whole of its nitrogen in the analytical process.

It is not possible to determine nitrogen in nitriles and in silver and alkali-metal nitrates; unreliable and variable results may be obtained also in the analysis of polynitro compounds, heterocyclic compounds, condensed-ring compounds, compounds with angular methyl groups, methylated amines, etc.

With the object of determining nitrogen in compounds of this sort, several modifications of the micro-Dumas method have been proposed recently [1-5]. Almost all these methods demand considerable complication of the apparatus and procedure, and even then they do not always give reliable results. It seemed to us quite probable that the actual method of combustion is the main source of the lack of success in the analysis of some classes of nitrogen-containing compounds, and that the use of enormous excesses of oxidizing and reducing agents in the Dumas method is based merely on an attempt to ensure adequate contact between the compound being analyzed and the incandescent part of the filling. If we could carry out the combustion in such a way as to ensure complete and adequately long contact of the compound with a small amount of oxidizing agent, and of the oxides of nitrogen formed with a small amount of reducing agent, then not only would the cumbersome filling of the combustion tube be unnecessary, but it might be possible to obtain quite acceptable results for compounds that cannot be analyzed at present by the Dumas method.

Martin [6] has carried out some interesting work in this direction. He proposed to free a part of the tube from filling. In the empty part of the combustion tube he placed a small test tube containing the weighed sample of substance covered with a layer of copper oxide, and he carried out the combustion in this test tube, gradually moving the burner from its open end to its closed end. Martin states that with such a method of combustion only gases pass to the filling. This method of decomposing the substance must be regarded as quite satisfactory. However, while removing part of the filling from the tube, Martin left the second half of the tube unchanged, i. e., there were still two layers of copper oxide with an intermediate layer of copper. Thus, there remained a layer of oxidizing agent to deal with possible incomplete combustion of the substance in the test tube; also, as previously, reduction of oxides of nitrogen was effected in the combustion tube with a large excess of reducing agent.

EXPERIMENTAL

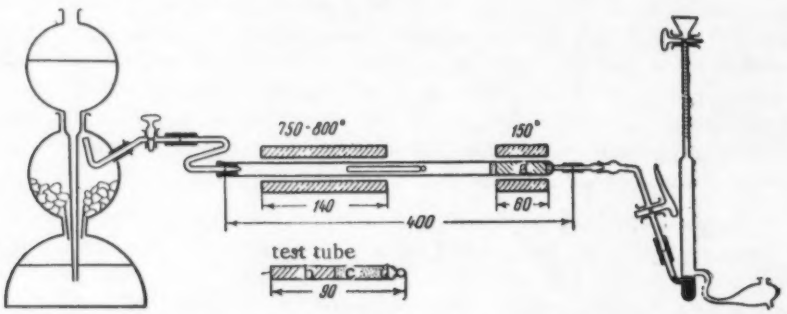
We concluded that the contact between the substance and the oxidizing agent was already adequate in the proposed technique of combustion and there was therefore no need for a supplementary layer of copper oxide in

the combustion tube. Also, it would be better to carry out the reduction of oxides of nitrogen in the same test tube. We therefore went further than Martin by freeing the tube from all filling apart from a short layer of hopcalite I, which was placed at the nitrometer end of the combustion tube. A layer of hopcalite 70 mm in length is quite sufficient for the complete oxidation of carbon monoxide at almost any possible rate of passage of gas through the apparatus. In order to make quite sure of the oxidation of difficultly combustible compounds, we added a little nickel oxide to the copper oxide. Hence, in the method that we propose, the combustion of the substance and the reduction of oxides of nitrogen are carried out in the test tube containing the sample, which is placed in an empty combustion tube. The oxidant used is a mixture of 100 parts of wire-form copper oxide and 1 part of nickel oxide powder; the reductant is copper wire previously reduced in a stream of hydrogen at 400-500°. As compared with the Dumas method, the amount of copper oxide is reduced to $^1/_{15}$, and the amount of reduced copper to $^1/_4$ of previous amount.

By the proposed method some of the defects of the generally accepted micro-Dumas method can be eliminated. Thus, in combustion by our method the gases leave the test tube gradually, after the combustion and reduction of oxides of nitrogen. The experimental results reported below show that we succeeded in effecting quite adequate contact with small amounts both of oxidant and of reductant. Also, the fact that in the combustion the furnace moves to meet the vapor of the substance results in conditions of combustion that are on the whole more favorable, because the vapor of the substance and the thermal-decomposition and combustion products pass not into a cold layer of filling, but into a hot layer, with which they react immediately. In the first place this accelerates combustion and, in the second, it eliminates the possibility of the distribution of the substance along the tube, which sometimes occurs in the Dumas method. This latter behavior probably plays an important part in the analysis of nitriles. In combustion in the test tube cuprous cyanide either is not formed or is destroyed quantitatively by the heating. The absence of large excesses of oxidant and reductant naturally eliminates the errors associated with these excesses; it makes it possible to manage with a small amount of copper oxide and it preserves the quartz tube from attack.

The proposed method was checked with numerous compounds. Good results were obtained in all cases; some of them are given in the table.

Our apparatus (see Figure) consists of a Kipp apparatus for the generation of carbon dioxide, a combustion tube 400 ml in length and 10 mm in internal diameter, in the nitrometer end of which is a layer of hopcalite 70 mm in length, a tap, a nitrometer containing 50% potassium hydroxide, and two furnaces. A furnace, 60 mm in length, maintains the layer of hopcalite at 150° throughout the working day. A second furnace, 140 mm in length, effects the combustion at 800°.



Scheme of apparatus (in mm): a) hopcalite, b) copper, c) copper oxide, d) copper oxide and nickel oxide with reducing agent.

The sample was placed in a quartz test tube, 90 mm in length and 5 mm in internal diameter. A 100:1 mixture of copper and nickel oxides was sprinkled onto the sample; the tube was shaken in order to mix the sample with the first portions of the mixture, and it was then rather more than half filled with mixture. The rest of the test tube was filled with reduced copper.* A given portion of copper can be used several times, since in practice only a small layer of it is oxidized. However, repeated roasting results in a change in the structure

* The reduction of copper oxide was carried out at 400-500° in a stream of hydrogen. The copper so prepared was sufficiently active.

No.	Substance	Nitrogen content (%)				
		calc.	found by proposed method	departure	found by Dumas method	departure
1	Silver nitrate	8.23	8.20	−0.03	7.20	−1.03
2	2-(Dimethylaminomethyl)-N,N-dimethylcyclohexylamine dipicrate	17.45	8.24 17.49 17.42	+0.01 +0.04 −0.03	6.39 12.74 17.50	−1.84 +0.29 +0.05
3	Decahydro-4-quinolinol hydrochloride	7.37	7.56 7.41	+0.17 +0.02	7.94 8.12	+0.57 +0.75
4	1-[2-(2-thienyl)ethyl]piperidine methiodide	4.38	4.47 4.26	+0.14 −0.07	3.89 3.86	−0.54 −0.47
5	3-[1-(bromoethynyl)cyclohexyloxy]propionitrile	5.47	5.61 5.56	+0.14 +0.09	—	—

of its surface and to reduction in its chemical activity. Hence, if the copper acquired a metallic luster it was necessary to replace it by a fresh portion.

The filled test tube was placed in the middle of the combustion tube with its open end toward the Kipp apparatus. Air was then displaced from the system by carbon dioxide in the way recommended in the micro-Dumas method. The tap of the Kipp apparatus was then closed, and a combustion furnace, heated to 750-800°, was applied to the combustion tube in such a way that the half of the test tube directed toward the Kipp apparatus was within the furnace. The nitrometer contained a solution of alkali. Wet cotton wool or ice was placed on the part of the combustion tube containing the closed end of the test tube. Such cooling is particularly useful in the analysis of volatile or readily decomposed substances. The combustion furnace was gradually moved toward the closed end of the test tube, i. e. toward the sample of the substance.

The rate of combustion was regulated by the movement of the furnace as in the Dumas method, i. e. so that one bubble separated in the nitrometer every two minutes. When the furnace had been moved to such an extent that the closed end of the test tube was in the hottest section and the evolution of bubbles in the nitrometer had stopped, displacement of the gases into the nitrometer was begun. The combustion furnace was removed only when this displacement was complete. The further operations and the calculation of results were the same as in the micro-Dumas method.

SUMMARY

1. A new variant of the micro-Dumas method was developed.

2. It was shown that there is no need to have any filling in the combustion tube apart from a short layer of hopcalite if the combustion is carried out in the test tube holding the sample; a short length of filling in the test tube can deal adequately with the complete oxidation of the compound and the reduction of oxides of nitrogen.

3. It was shown that good analytical results can be obtained by the proposed method (accurate within ± 0.2%), even with compounds that do not readily undergo complete combustion.

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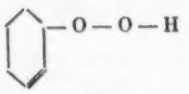
KINETICS OF THE CATALYTIC REDUCTION OF PEROXIDES AND HYDROPEROXIDES

COMMUNICATION 2. HYDROGENATION OF BENZOYL PEROXIDE, tert-BUTYL PEROXYBENZOATE, AND 2-CYCLOHEXEN-1-YL HYDROPEROXIDE

A. A. Balandin, L. Kh. Freidlin, and N. V. Nikiforova

In the previous communication [1], in which we studied α,α-dimethylbenzyl hydroperoxide ("cumene hydroperoxide"), α,α-dimethylbenzyl ethyl peroxide, and 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide, we showed that organic peroxy compounds readily undergo hydrogenolysis over a nickel catalyst; this behavior is in accord with multiplet theory. We found also that the structure of the peroxy compound has a considerable effect on the rate of reaction. In the present paper we describe the kinetics of the hydrogenolysis of benzoyl peroxide (I) and tert-butyl peroxybenzoate (II) over nickel and of 2-cyclohexen-1-yl hydroperoxide (III) over Ni, Pd, and Pt:

(I) (II)



(III)

In this way we supplemented our information on the effect of structure on catalytic reactivity. At the same time the succession of reactions of these substances over Ni can be followed experimentally and compared with the sequence previously deduced theoretically on the basis of the multiplet theory. The present experiments show that only the O–O bond is broken in compounds (I) and (II). The observed low strength of this bond over nickel is in accord with theory because $-E$ for O–O ($-E = -14$) is less than the values for the other interatomic bonds in the molecules (I) and (II): $-E = 10$ for C = O; $-E = 20$ [2] for the benzene bond; $-E = 17$ for C – O; $-E = 48.5$ for C – C ($-E$ is the height of the energy barrier in kilocalories).

In the case of the hydrogenation of 2-cyclohexen-1-yl hydroperoxide (III) we are able for the first time to compare the ease of rupture of the peroxide bond O – O with that of the π-bond of C=C in presence of hydrogen over nickel. Experiment shows that here also the peroxide bond reacts first, which is in full accord with the multiplet theory, for in hydrogenation $-E = -14$ for the O – O bond and $-E = 2.9$ for the π-bond of C C.

Actually, according to the equations of the multiplet theory, for a group of atoms reacting in contact with the catalyst

$$\begin{array}{l} -O\ \ H \\ \ \ |\ \ \ | \\ -O\ \ H \end{array} \rightarrow M \rightarrow \begin{array}{l} -O-H \\ \\ -O-H \end{array}$$

the heats of formation E' and of decomposition E" of the multiplet complex M over nickel will be

$$E_1' = -Q_{O-O} - Q_{H-H} + 2Q_{O-Ni} + 2Q_{H-Ni} =$$
$$= -47 - 104{,}2 + 2 \cdot 48{,}5 + 2 \cdot 55 = 55{,}8;$$
$$E_1'' = 2Q_{O-H} - 2Q_{O-Ni} - 2Q_{HNi} = 2 \cdot 110{,}6 - 2 \cdot 48{,}5 - 2 \cdot 55 = 14{,}2,$$

and for the group of atoms

$$\begin{array}{l} >C\ \ H \\ \ \ \|\ \ \ | \\ >C\ \ H \end{array} \rightarrow M' \rightarrow \begin{array}{l} >C-H \\ \ \ | \\ >C-H \end{array}$$

they will be

$$E_2' = -Q_{C=C} - Q_{H-H} + 2Q_{-CNi} + 2Q_{HNi} =$$
$$= -46{,}7 - 104{,}2 + 2 \cdot 19 + 2 \cdot 55 = -2{,}9;$$
$$E_2'' = 2Q_{C-H} - 2Q_{-CNi} - 2Q_{HNi} = 2 \cdot 90{,}5 - 2 \cdot 19 - 2 \cdot 55 = 30{,}1.$$

in which Q is the bond energy, the numerical values of which are taken from [3].

The rate of the first reaction is determined by the value of $-E_1'' = -14.2$, since it is less than E_1', and the rate of the second reaction is determined by the barrier $-E_2' = 2.9$, since it is less than E_2''. According to the multiplet theory, however, the one for which $-E$ is the lower goes the more readily. Here $(-E_1'') < (-E_2')$, so that according to theory the peroxide bond O–O should react with hydrogen over nickel more readily than the π-bond of C = C. Experiment confirms this theoretical inference.

EXPERIMENTAL

Preparation of 2-Cyclohexen-1-yl Hydroperoxide. The structure of "cyclohexene hydroperoxide" (2-cyclohexen-1-yl hydroperoxide) was established by Hock and Schrader [4] and by Griegee [5]. Numerous methods of preparation are given in the literature [4-14]. Almost all of the methods amount to the oxidation of cyclohexene with molecular oxygen or air. In most cases reference is made to the lengthy oxidation process and the low yields of the hydroperoxide. Thus, Hock and Schrader [4] report that, after shaking cyclohexene with oxygen in a flask for 200 hours at 30-35°, they obtained a yield of hydroperoxide of less than 20%. Griegee and co-workers [5] carried out the same process photochemically in a quartz flask and so shortened the reaction time to 24 hours.

Methods of thermal and photochemical autooxidation without use of initiators or catalysts are inconvenient owing to the relative complexity of the apparatus, the long duration of the process, and the low yields. One of the first references to the use of catalysts in the oxidation is contained in a British patent [12], which reports the use as catalysts of heavy-metal compounds (Mn, V, Co, Pb, Fe, Ni, Cu, Cr, and Hg compounds), namely their oxides or hydroxides, or organic salts soluble in the substance being oxidized. In this method 0.15-0.8% of catalyst is taken, temperatures of up to 45° are used, the duration of reaction is about 20 hours, and the yield is 19-30%.

With some slight modifications we used the method [13] in which the oxidation of cyclohexene is effected with molecular oxygen in presence of cobalt stearate. Extremely pure cyclohexene 60 g; [b.p. 82.5° (758 mm); n_D^{21} 1.4450] was placed in a hydrogenation flask, 0.2 g of cobalt stearate was added, and oxygen was passed into the flask after first passing through vessels containing 50% KOH, calcium chloride and soda-lime, and calcium chloride and phosphoric oxide. The flask was maintained at 45° and was agitated in a shaker. The process lasted six hours (according to the oxygen uptake the yield of oxidized product was about 25%), and the product was then vacuum-fractionated. A fraction of b.p. 60-65° (1 mm) was taken; the product accumulated and was fractionated at 0.1 mm. The resulting peroxy preparation had b.p. 48° (1 mm); n_D^{20} 1.4908; d_4^{20} 1.0600.

It must be pointed out that the preparation of pure 2-cyclohexen-1-yl hydroperoxide presents considerable difficulty owing to its instability under the usual conditions [4, 5, 11]. This fact explains the variation in the values of the constants of this substance given in the literature: b.p. 48-50° (0.3 mm); d_4^{20} 1.051[4]; b. p. 51° (0.3 mm); d_4^{20} 1.0588; n_D^{20} 1.4831 [5]; b. p. 48° (0.1 mm); d_4^{20} 1.0638; n_D^{20} 1.4900 [10]; b. p. 65° (1 mm); d_4^{20} 1.0537; n_D^{20} 1.4898 [13]; b. p. 20° (10^{-4} mm); n_D^{20} 1.4896 [6]; b. p. 66-67° (2 mm); n_D^{20} 1.4887; d_{20}^{20} 1.0310-1.0400 [11]. Although keeping in the air at room temperature results in rapid decomposition of the hydroperoxide, it was found that it is stable for a period of months when kept in a Pyrex flask at not above – 5°.

Pure benzoyl peroxide was prepared by purification of the commercial product: two recrystallizations from cold chloroform-methanol [15] followed by vacuum drying. The preparation of tert-butyl peroxybenzoate was kindly supplied by Meshcheriakov; it had the following constants: b. p. 84° (3 mm); n_D^{20} 1.4990; d_4^{20} 1.0413

Found %: C 68.00; H 7.24

$C_{11}H_{14}O_3$. Calculated %: C 68.04; H 7.22

Method of Analysis. In the determination of active oxygen in the peroxy compounds, the iodometric and stannometric methods described in [14] gave extremely low results in comparison with the total amount of hydrogen required in the hydrogenation of the same weight of peroxy compound. For benzoyl peroxide good results were obtained by a modification of Wibaut's method [16]. The procedure for this method is given below.

Sodium bicarbonate (1.5 g) and commercial glacial acetic acid (20 ml) were introduced into a 250-ml conical flask having a glass joint which connected it to a tap and to a trap containing water. A little flask containing the benzoyl peroxide solution (about 0.4 mmole of pure substance) was placed in a vertical position in the large flask containing acetic acid solution. A solution of 2 g of potassium iodide (5 ml) was then added to the acetic acid in the large flask, which was then connected to the trap. When the evolution of carbon dioxide ceased, the contents of the small flask were mixed with shaking with the CH_3COOH–KI solution. The mixture was kept in the dark for ten minutes at 70°, and 50 ml of water was added; it was titrated with 0.05 N $Na_2S_2O_3$ with addition of 5 ml of starch solution at the end of the titration. The total amount of hydrogen required for the hydrogenation of a sample of the peroxide corresponded to the peroxide content determined analytically.

No reliable methods for the analysis of unsaturated peroxides have been described in the literature. The determination of 2-cyclohexen-1-yl hydroperoxide by Wibaut's method [16] gave results which did not correspond at all to the total amount of hydrogen required for hydrogenation. For the analysis of this hydroperoxide we used a modification of Barnard's stannometric method [6]. The procedure was as follows: 1 ml of the solution to be investigated, which contained about 0.75 mg-equivalent of the hydroperoxide, was added to 10 ml of commercial glacial acetic acid in a 250-ml round-bottomed flask to which a tap was attached through a ground glass joint. Rapid addition was then made of 15 ml of 0.1 N $SnCl_2$ from a buret, and the flask was quickly evacuated down to 20 mm and filled with nitrogen, then again evacuated and again filled with nitrogen. The flask was left at room temperature for one hour, and addition was then made of a boiling solution containing 5 ml of a solution of ferric alum (200 g in 1 liter of water), 1 g of NH_4Cl, and 45 ml of water. The mixture was heated at 75° in a water bath for 30 seconds and cooled rapidly; 10 ml of a solution of phosphoric and sulfuric acids was then added (75 ml H_3PO_4 + 75 ml H_2SO_4 + 350 ml H_2O). Ferrous iron was titrated with 0.05 N $K_2Cr_2O_7$ in presence of 10 drops of diphenylamine solution as indicator (1% solution of diphenylamine in concentrated H_2SO_4). The end point was marked by a sharp change from green to violet. The content of 2-cyclohexen-1-yl hydroperoxide, as determined by Barnard's method, was 80-83%. With tert-butyl peroxybenzoate and α,α-dimethylbenzyl hydroperoxide Barnard's method gave results in accord with theory.

The hydrogenation of the peroxy compounds and the preparation of the catalysts was carried out by the procedure described in [1]. All volumes of hydrogen were reduced to STP. A fresh portion of catalyst was taken for each experiment. The flask was placed in a thermostat. In all experiments the rate of shaking was 1000 per minute. The order of the reaction and the rate constant were determined from the main part of the kinetic curve. Control experiments with benzoyl peroxide and tert-butyl peroxybenzoate showed that, in absence of catalysts, the peroxy compounds investigated are stable under the experimental conditions.

Hydrogenation of Benzoyl Peroxide. Benzoyl peroxide is sparingly soluble in alcohols, dioxane, anisole, and dibutyl ether; a solution in benzene was therefore prepared. For each experiment 0.44 g of the peroxide was taken as a solution in 20 ml of benzene. Hydrogenation was carried out in presence of 0.5 g of Raney nickel. It was found that, when several experiments were carried out in succession over the same portion of catalyst, the rate of reaction fell. In every experiment, therefore, a fresh portion of catalyst was used. In all experiments the theoretical amount of hydrogen was absorbed.

As will be seen from Fig. 1, the hydrogenation of benzoyl peroxide over Raney nickel follows a first-order equation. Figure 1 (a-e) gives kinetic curves for the hydrogenation of benzoyl peroxide at 5, 10, 15, 20, and 25°. With rise in temperature the rate of reaction rises. The rate constants are 0.100, 0.121, 0.144, 0.176, and 0.211 $minute^{-1}$, respectively. The apparent activation energy in the range 5-25° is approximately 6.5 kcal/mole (Fig. 1f).

We found previously [1] that, when the catalyst was saturated with hydrogen in alcohol and then used for hydrogenation in benzene or cyclohexane, the hydrogenation curve had the character of the curve for hydrogenation in an alcohol medium. For this reason we carried out the hydrogenation of benzoyl peroxide in benzene solution after first saturating the catalyst with hydrogen in alcohol.

The hydrogenation results are shown in Fig. 1g. It will be seen that in this case reaction is of zero order. The rate constants at 5, 10, 15, and 25° are 3.5, 4.0, 5.5, and 8.2 ml/minute, respectively, and the apparent activation energy in the range 5-25° is about 7.2 kcal/mole (Fig. 1h).

Hydrogenation of tert-Butyl Peroxybenzoate. The hydrogenation of tert-butyl peroxybenzoate was carried out in presence of 0.5 g of Raney nickel. For each experiment, 0.584 g of the peroxy compound was taken in 15 ml of ethanol. The kinetic curves for the hydrogenation of tert-butyl peroxybenzoate at 6.5, 11, 16, 20, and 35° are given in Fig. 2a. The rate constants are 0.0706, 0.0811, 0.119, 0.160, and 0.230 $minute^{-1}$, respectively. The apparent activation energy in the range 6.5-20° is about 9.4 kcal/mole (Fig. 2b). The theoretical amounts of hydrogen were absorbed.

Hydrogenation of 2-Cyclohexen-1-yl Hydroperoxide. As catalyst, apart from Raney nickel we used palladium black that had been kept in the air for 13 months, platinum black that had been kept in the air for six months (Sample 1), and platinum black prepared immediately before use (Sample 2). As solvent we used 96% ethanol (15 ml for each experiment). The amount of the hydroperoxide taken for each experiment was 0.203-0.212 g, the content of pure hydroperoxide being 82.8% (by analysis). The total amount of hydrogen used in the hydrogenation of the hydroperoxide corresponded to that required for reduction to cyclohexanol. Thus, in the hydrogenation of 0.212 g of the hydroperoxide in presence of 0.5 g of Raney nickel, the amounts of hydrogen absorbed in a series of experiments were 66.9, 73.3, 71.6, 72.6, 73.8 ml (STP) (theoretical amount 69 ml).

The kinetic curve for the hydrogenation of 2-cyclohexen-1-yl hydroperoxide (0.212 g) in presence of 0.5 g of Raney nickel is given in Fig. 3a. Experiments were carried out in which, after the absorption of 28.5, 31.7, 35.9, 40.1, and 50 ml (STP) of hydrogen, 0.5-ml samples of the solution were taken from the flask and added to a very sensitive reagent for peroxy compounds, namely thiocyanate [15], with which even traces of peroxy compound can be detected. It was found that in the first place the hydroperoxy group is hydrogenated, and then the double bond; but the rate of hydrogenation of the double bond in very much greater than the rate of hydrogenation of the hydroperoxy group. Both functional groups are hydrogenated according to a zero-order equation, so that the rates are equal to the rate constants. However, these constants, as the theory of hydrogenation shows [17], contain adsorption coefficients as well as true rate constants k.

The question arises of which of these two reactions has the higher true rate constant. The theory of hydrogenation [17] considers two kinds of active centers: those which activate the substance being hydrogenated and those which activate hydrogen. According to this theory, in a mixture of two unsaturated compounds, the one

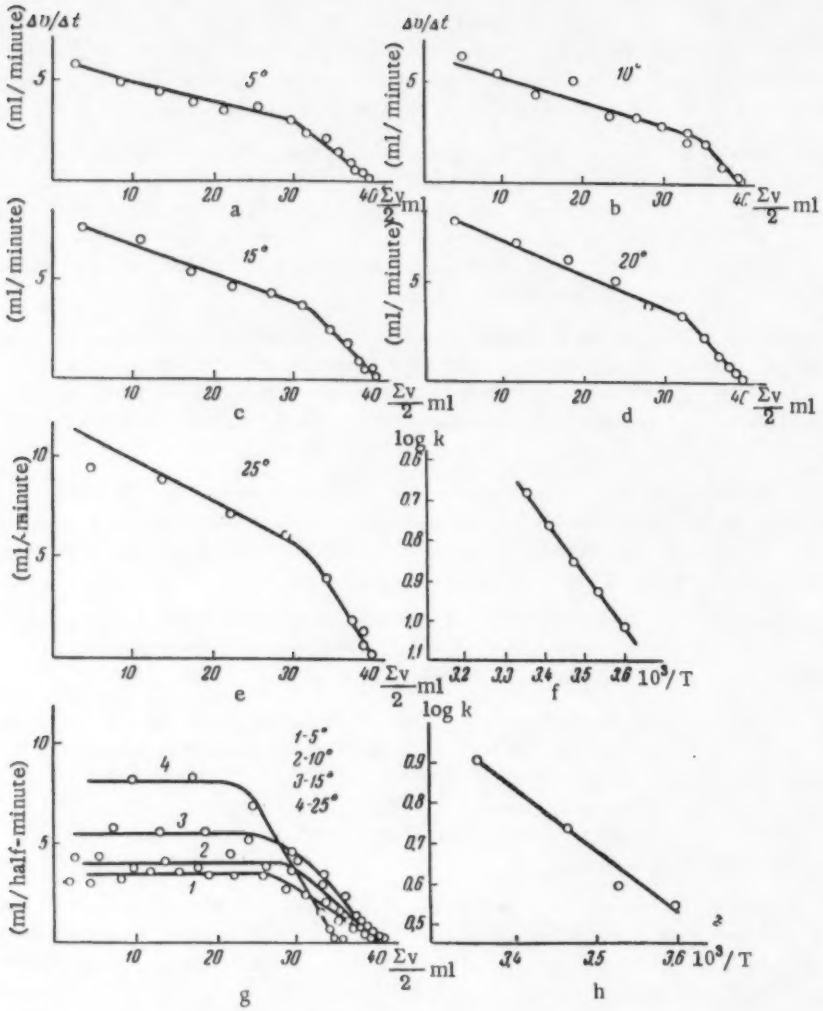


Fig. 1. Hydrogenation of benzoyl peroxide over a nickel catalyst: a) to e) kinetic curves for the hydrogenation of the peroxide in benzene at various temperatures; f) activation energy for the hydrogenation of the peroxide in benzene; g) kinetic curves for the hydrogenation of the peroxide in benzene + ethanol; h) activation energy for the hydrogenation of the peroxide in benzene + ethanol.

that hydrogenates first is that for which $\underline{kb'}$ is the higher ($\underline{b'}$ is the adsorption coefficient of the substance undergoing hydrogenation for the centers that activate it). However, the rate constant for the reaction is more sensitive to change in the nature of the molecule than the tendency to be adsorbed. Variation in the value of $\underline{kb'}$ among various compounds must therefore be determined mainly by the value of $\underline{k}$. Thus, experiment shows that, on nickel, the true rate constant k_1 for the hydrogenolysis of the peroxide bond is greater than the true rate constant k_2 for the hydrogenolysis of the olefin bond. This is in full accord with the predictions of the multiplet theory (see introduction).

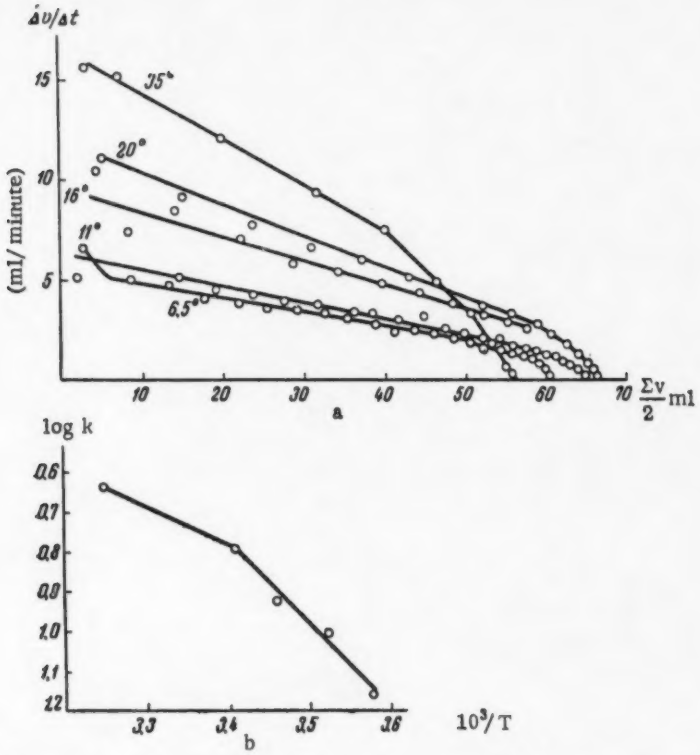


Fig. 2. Hydrogenation of tert-butyl peroxybenzoate over nickel: a) kinetic curves for hydrogenation at various temperatures; b) activation energy for the hydrogenation of the peroxy compound.

The actual reaction rates of zero order of two compounds, as distinct from the rate constants, are related to one another as follows [17]:

$$\frac{v_1}{v_2} = \frac{k_1 b_1'}{k_2 b_2'} \cdot \frac{b_2 - c_2}{b_1 - c_1}, \qquad (1)$$

in which b and c are adsorption coefficients of the substance being hydrogenated and the reaction product, respectively, for centers which activate hydrogen; the subscripts indicate to which compound (first or second) the given quantities refer. Thus, the rate of the first reaction may be either higher or lower than that of the second. If $k_1 b_1' > k_2 b_2'$, then the rate of the second reaction v_2 will be higher than v_1 when the extent to which the tendency for the substance being hydrogenated to be adsorbed at centers that activate hydrogen exceeds the corresponding tendency of the reaction product is appreciably greater for the first substance than for the second. Actually, it follows from Equation (1) that

$$\frac{v_1}{v_2} < 1, \quad \text{if} \quad \frac{b_1 - c_1}{b_2 - c_2} > \frac{k_1 b_1'}{k_2 b_2'}. \qquad (2)$$

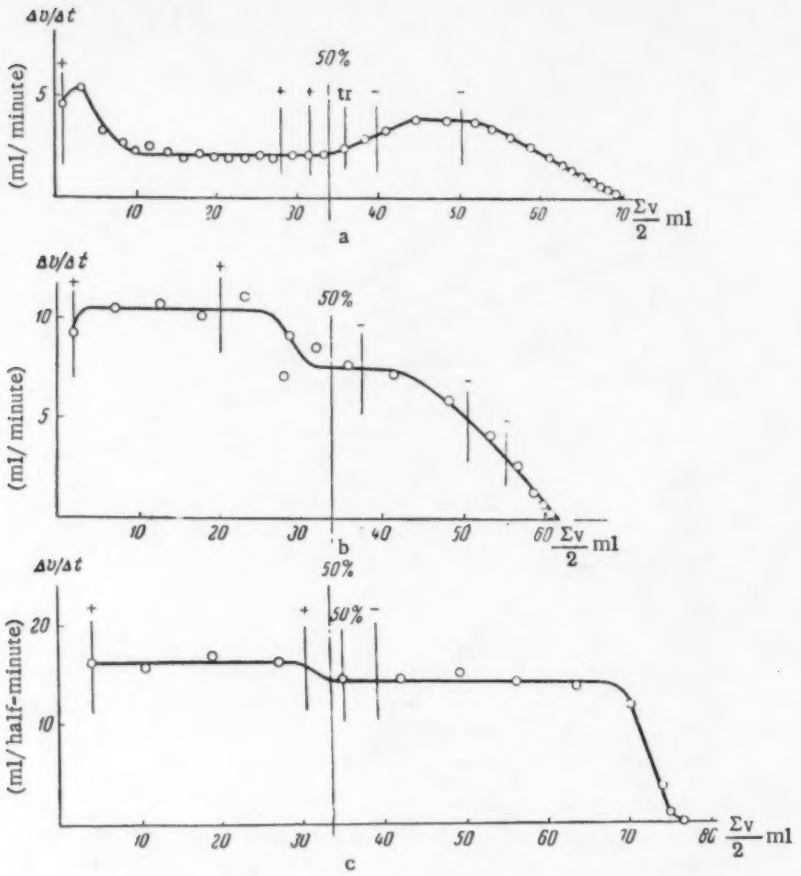


Fig. 3. Sequence of hydrogenation of functional groups in 2-cyclohexen-1-yl hydroperoxide: a) over Raney nickel; b) over Pd black; c) over Pt black (+)peroxide detected; tr) traces of peroxide;–) no peroxide).

In these considerations we are quite justified in replacing a mixture of two substances having different reactive functional groups by a single substance which contains both of these groups, which will be characterized by different probabilities of attachment to the surface of the catalyst, these probabilities being dependent on the tendencies of the groups to undergo adsorption, i. e., proportional to their adsorption coefficients. Also, one of the two reactions may be not hydrogenation, but hydrogenolysis, because the doublet schemes of these two reactions are very similar (see above). It is interesting that on a surface that activates hydrogen the difference between the adsorption coefficients of the peroxy compounds (b_1) and the alcohol (c_1) is greater than in the case of the olefin (b_2) and the paraffin (c_2) [compare Equation (2)]. It is possible that this is to be explained by the presence of two adsorptionally active oxygen atoms in the peroxide molecule, whereas there is only one oxygen atom in the alcohol molecule.

In the hydrogenation of 2-cyclohexen-1-yl hydroperoxide over Pd black (0.1 g) the same sequence was observed for the hydrogenation of the functional groups as in the case of nickel. The rate of hydrogenation of the double bond was lower than the rate of hydrogenation of the peroxy group. The kinetic results are given in Fig. 3b. In the hydrogenation of 2-cyclohexen-1-yl hydroperoxide in presence of 0.1 g of Pt black (Sample 1), the same sequence for the hydrogenation of the functional groups was again observed; the rate of hydrogenation of the double bond was somewhat lower than for the peroxide group (Fig. 3c). In all cases there was a distinct break in the curve at the point at which hydrogenation of the peroxide group ended and that of the double bond began.

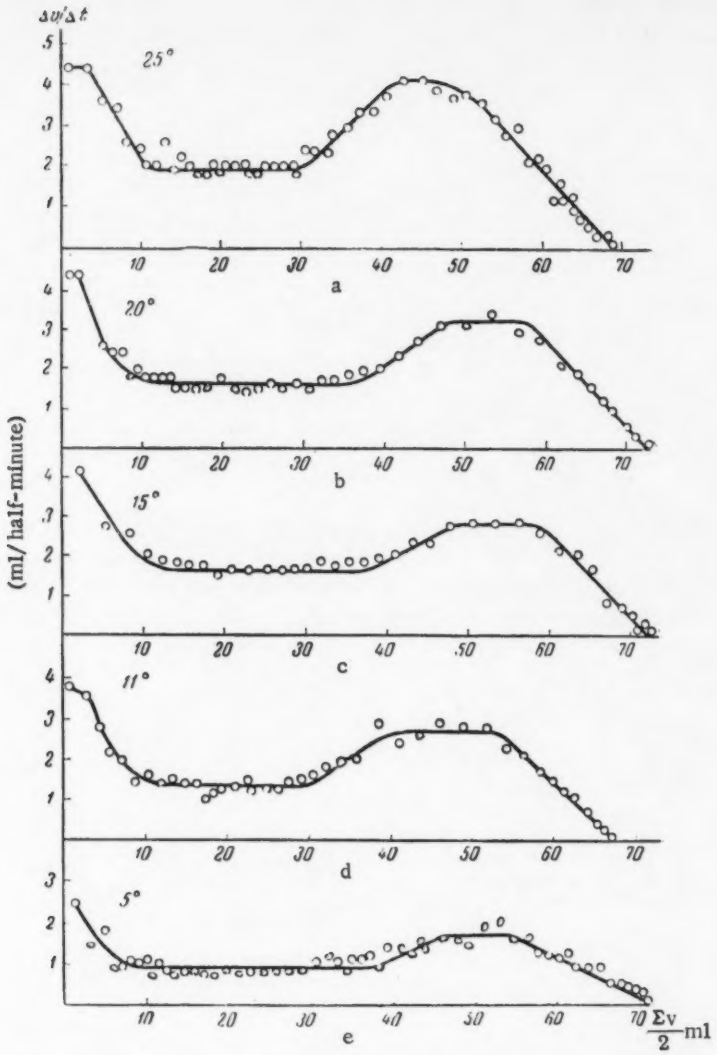


Fig. 4. Kinetic curves of the hydrogenation of 2-cyclohexen-1-yl hydroperoxide on nickel at various temperatures.

Effect of Temperature on the Rate of Hydrogenation of 2-Cyclohexen-1-yl Hydroperoxide over a Nickel Catalyst. Hydrogenation of the hydroperoxide was carried out in presence of 0.5 g of Raney nickel at 5, 11, 15, 20, and 25°. The kinetic curves are given in Fig. 4. The respective rate constants are 1) for the peroxide group 0.9, 1.35, 1.55, 1.6, and 1.9 ml/half-minute, and 2) for the double bond 1.7, 2.65, 2.8, 3.2, and 4.1 ml/half-minute. Apparent activation energies in the range 5-25° calculated from these results are 5.0 kcal/mole for the peroxide group and 7.3 kcal/mole for the double bond (Fig. 5).

Hydrogenation of 2-Cyclohexen-1-yl Hydroperoxide over Palladium and Platinum Blacks. First, experiments were carried out to determine the stability of Pd and Pt blacks in a series of successive experiments. In a series of four experiments with a given portion (0.1 g) of Pt black (Sample 1) it was found that its activity remained constant only in the first two experiments, after which it began to fall. After each experiment the

catalyst (Pd or Pt black) was washed twice with distilled ether (15 ml portions) and twice with ethanol (15 ml portions); it was saturated with hydrogen in alcohol in the usual way for 20 minutes.

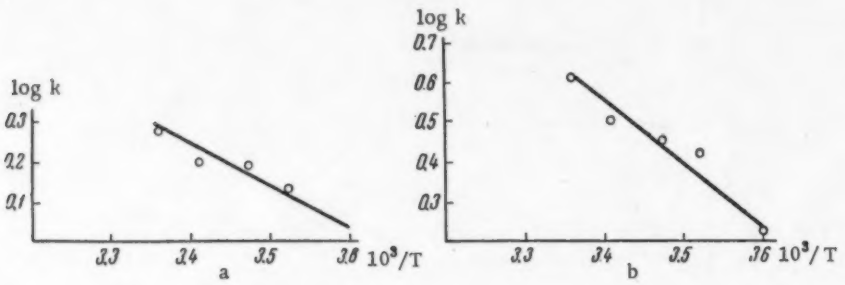


Fig. 5. Activation energy for the hydrogenation of 2-cyclohexen-1-yl hydroperoxide: a) for the peroxide group; b) for the double bond.

The hydrogenation of 2-cyclohexen-1-yl hydroperoxide in presence of 0.1 g of Pt black (Sample 1) was carried out at 6, 11, 15, and 25°. The kinetic curves are given in Fig. 6a. The respective rate constants are 9.7, 12.4, 15.0, and 16.5 ml/half-minute for the peroxide group and 7.0, 8.25, 11.7, and 14.2 ml/half-minute for the double bond. The apparent activation energy in the range 6-25° is about 5.3 kcal/mole for the peroxide group and 14.4 kcal/mole for the double bond (Figs. 6b and 6c).

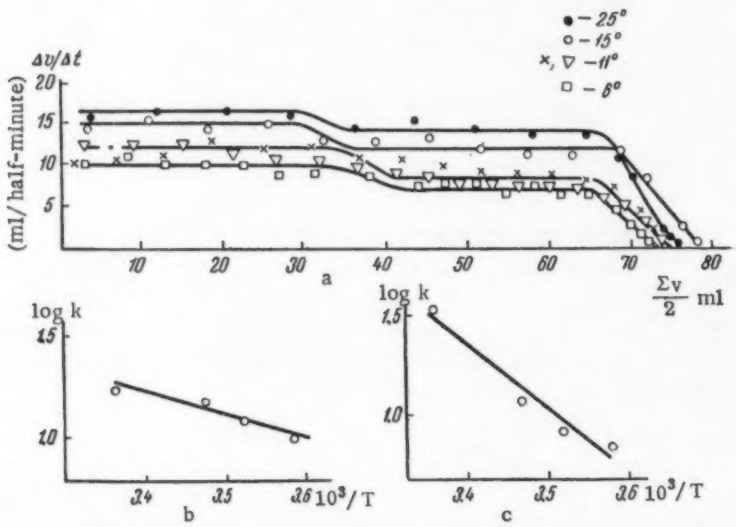


Fig. 6. Hydrogenation of 2-cyclohexen-1-yl hydroperoxide over Pt black (Sample 1): a) kinetic curves for hydrogenation at various temperatures; b) activation energy for the hydrogenation of the peroxide group; c) activation energy for the hydrogenation of the double bond.

In the hydrogenation of 2-cyclohexen-1-yl hydroperoxide in presence of Pt black (Sample 2) (0.1 g) under the same conditions as for Sample 1, the kinetic curve had no break at the point of complete hydrogenation of the peroxide group. The rate of hydrogenation remained constant throughout the whole process; the reaction

was of zero order, and the rate constant at 5° was 3.4 ml/half-minute. Several experiments were carried out with 0.05 g samples of Pt black. In all experiments reaction was at constant rate for both functional groups.

The hydrogenation of 2-cyclohexen-1-yl hydroperoxide (0.212 g) was carried out at 10, 15, and 20°. The respective rate constants are 4.5, 5.0, and 5.2 ml/half-minute. The apparent activation energy calculated from these results is 2.5 kcal/mole.

A summary of our results on the kinetics of the hydrogenation of organic peroxy compounds over nickel is given in the table, in which the results from the investigation [1] are also included.

Kinetics of the Hydrogenation of Peroxy Compounds over Nickel

Peroxy compound	Solvent	Hydrogenation temperature (°C)	Rate constant (ml/min per g of catalyst)	Apparent activation energy (kcal/mole)
Zero-order reactions				
α,α-Dimethylbenzyl hydroperoxide	Ethanol	5	13.3	
		20	25.3	5.0
		30	33.3	
α,α-Dimethylbenzyl ethyl peroxide		8	17.0	
		15	23.0	5.4
		25	29.0	
1,2,3,4-Tetrahydro-1-naphthyl hydroperoxide	Benzene	20	5.2	
		5	14.0	
Benzoyl peroxide	Benzene + ethanol	10	16.0	7.2
		15	22.0	
		25	32.8	
2-Cyclohexen-1-yl hydroperoxide	Ethanol	5	3.6	
		11	5.4	
		15	6.2	5.0
		20	6.4	
		25	7.6	
First-order reactions			(minute^{-1} per gram of catalyst)	
1,2,3,4-Tetrahydro-1-naphthyl hydroperoxide	Methanol	20	1.72	
Benzoyl peroxide	Benzene	5	0.20	
		10	0.242	
		15	0.288	6.5
		20	0.352	
		25	0.422	
tert-Butyl peroxybenzoate	Ethanol	6.5	0.141	
		11	0.162	
		16	0.238	9.4
		20	0.320	
		35	0.460	
tert-Butyl peroxide	"	20—50	Not hydrogenated	

The following conclusions can be drawn from the table. The reactions fall into two groups: zero-order and first-order reactions. Within each of these groups the structure of the peroxy compound has generally little effect on the observed rate constants per gram of nickel, which at 20° vary roughly from 5 to 30 ml/minute for zero-order reactions and from 0.3 to 1.7 minute^{-1} for first-order reactions. The effect of temperature is well marked but, in accordance with theory, the apparent activation energy ϵ is low (5-7 kcal/mole). The nature of the solvent greatly affects the course of reaction. Thus, in benzene the hydrogenation of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide is a zero-order reaction, whereas in methanol it is a first-order reaction. Peroxy compounds containing the tert-butyl radical differ from the others. Thus, tert-butyl peroxybenzoate has a high activation energy (ϵ = 9.4 kcal/mole), and the activation energy for tert-butyl peroxide appears to be so great that under the given conditions the hydrogenation of this peroxy compound is not observed.

SUMMARY

1. An investigation was made of the kinetics of the hydrogenation of benzoyl peroxide and of tert-butyl peroxybenzoate over nickel and of 2-cyclohexen-1-yl hydroperoxide over nickel, palladium, and platinum.

2. It was shown that, in presence of nickel, first the peroxide group is hydrogenated, and then the double bond. This is in accord with deductions from the multiplet theory. The same sequence is observed over palladium and platinum.

3. Determinations were made of reaction order, rate constant, and activation energy for these processes.

4. The hydrogenation of peroxy compounds can serve as a catalytic method of preparing unsaturated alcohols.

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VAPOR-PHASE HYDROLYSIS OF HALOBENZENES OVER A PROMOTED PHOSPHATE CATALYST

L. Kh. Freidlin, A. A. Balandin, and G. A. Fridman

It was shown in a previous communication that, like silica gel, tricalcium phosphate is an active, stable, single-component catalyst for the vapor-phase hydrolysis of chlorobenzene [1]. It was suggested that the activities of the two catalysts are similar in nature. If so, it would be expected that the phosphate catalyst would also be promoted by cupric chloride.

The results of the present investigation confirmed this supposition. The optimum concentration of cupric chloride in the phosphate catalyst was determined and compared with the minimum concentration necessary for the promotion of silica gel. The existence of a common mechanism for the activating actions of silica gel and phosphate is confirmed also by the fact that over both catalysts the reactivities of chloro-, bromo-, and iodobenzenes diminish in the same order: $C_6H_5Cl > C_6H_5Br > C_6H_5I$.

EXPERIMENTAL

We have already given a detailed description of the experimental procedure [2]. The reaction was carried out by the flow method. The proportions by weight of halobenzene and water taken for reaction were approximately equal. Phenol was determined bromometrically. The yields of phenol and acid are given as percentages of the theoretical amounts on the basis of the amount of halobenzene passed.

TABLE 1

Effect of the Cupric Chloride Content of the Phosphate on the Hydrolysis of Chlorobenzene at Various Temperatures (Space velocity 0.3)

Experiment	Cupric chloride content of catalyst (%)	Temperature (°C)	Yield (%)		Experiment	Cupric chloride content of catalyst (%)	Temperature (°C)	Yield (%)	
			C_6H_5OH	HCl				C_6H_5OH	HCl
	0.0	450	4.2	—	9	0.0	550	8.1	6.4
1	0.1	450	16.9	7.0	9	0.5	550	40.4	46.6
2	0.1	500	22.0	21.5	10	1.0	450	17.1	22.5
3	0.5	350	2.2	2.5	11	2.0	450	19.2	25.9
4	0.5	400	8.4	9.3	12	2.0	500	26.4	43.8
5	0.5	450	22.2	22.2	13	2.0	550	27.2	60.1
6	0.5	450	20.5	22.7	14	8.0	450	7.5	46.5
7	0.0	500	5.6	0.9	15	8.0	500	6.2	59.8
7	0.5	500	38.1	43.3	16	8.0	550	7.8	64.9
8	0.5	500	34.9	39.9					

The catalyst was prepared by impregnation of tricalcium phosphate with aqueous cupric chloride and evaporation on a water bath. The paste obtained was formed into spheres, 3-4 mm in diameter, and dried at 125-150°. The catalyst was regenerated by treatment with air for 3-5 hours at 475-500°. The duration of the

experiment was one hour. In the tables the space velocity is expressed in grams per liter of catalyst per hour.

The experiments listed in Table 1, in which the cupric chloride content of the phosphate was constant, were all carried out with one portion of catalyst. In each of the experiments listed in Table 2 a fresh portion of catalyst was used. The same catalyst was used in the experiments listed in Tables 3, 4, and 5.

TABLE 2

Regenerating Effect of Cupric Chloride on Phosphate Catalyst Deactivated by Mineral Impurities (Temperature of experiments 500°; space velocity 0.3)

Experiment	Catalyst	Yield (%)	
		C_6H_5OH	HCl
1	Phosphate + $CuCl_2$ (0.5%)	38.1	43.3
2	Phosphate + NaCl (8%)	0.5	1.8
3	Phosphate + NaCl (8%) + $CuCl_2$ (0.5%)	4.3	6.1
4	Phosphate + Lead acetate (36%)	0.4	0.8
5	Phosphate + Lead acetate (36%) + $CuCl_2$ (0.5%)	2.5	2.4

TABLE 3

Productivity of the Phosphate Catalyst Promoted with 0.5% of $CuCl_2$ for Different Space Velocities of Passage of Chlorobenzene (Temperature of experiments 450°)

Experiment	Space velocity	Yield of C_6H_5OH	
		(%)	g/liter · hour
1	157	27.1	35.4
2	294	22.2	54.1
3	291	20.5	49.9
4	566	16.8	79.4
5	633	15.2	80.6
6	797	13.9	92.5
7	897	13.6	102.3

Hydrolysis of Chlorobenzene over a Phosphate Catalyst Promoted with Cupric Chloride. Table 1 shows the effect of the cupric chloride content of the phosphate on the activity of the catalyst in the hydrolysis of chlorobenzene at various temperatures. Figure 1 gives curves for the yields of phenol from chlorobenzene on promoted and unpromoted phosphate. It will be seen from Table 1 and Fig. 1 that the activity of a phosphate catalyst is greatly increased by an addition of cupric chloride. In presence of such a catalyst the hydrolysis of chlorobenzene proceeds at a measurable rate already at 350°, and at 450° the yield attains 22.2%. For comparison purposes, the curve for the activity of silica gel promoted with cupric chloride is also given in Fig. 1. The comparison shows that the activity of promoted phosphate is greater than that of promoted silica gel.

Figure 2 shows the ratio of the activity of catalyst promoted with cupric chloride (0.5%) to that of unpromoted catalyst: Curve 1 for silica gel, and Curve 2 for phosphate. Comparison of the curves shows that this ratio is considerably greater for the phosphate catalyst than for silica gel. Phosphate, therefore, is more strongly promoted by cupric chloride than silica gel is.

As will be seen from Fig. 3, the cupric chloride content of the phosphate catalyst has a great effect on the rate and course of the process. With increase in the cupric chloride content of the catalyst from 0.1 to 0.5%, catalyst activity increases appreciably. However, further increase in the cupric chloride content to 1, 2, 4, or 8% results in a continuous fall in the yield of phenol. Thus, with increase in the cupric chloride content of the

catalyst from 0.5 to 8% the yield of phenol is reduced

from 22.2	to	7.5%	at	450°
from 38.1	to	6.2%	at	500°
from 40.4	to	7.8%	at	550°

In these experiments the yield of hydrochloric acid is simultaneously greatly increased, namely

from 22.2	to	46.5%	at	450°
from 43.3	to	59.8%	at	500°
from 46.6	to	64.9%	at	550°

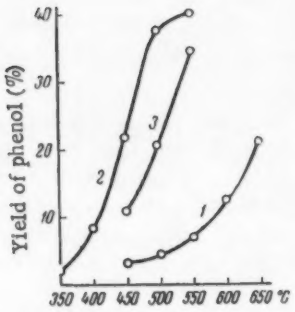

Fig. 1

Fig. 1. Vapor-phase hydrolysis of chlorobenzene in presence of tricalcium phosphate promoted with cupric chloride at various temperatures: 1) phosphate; 2) phosphate + 0.5% $CuCl_2$; 3) silica gel + $CuCl_2$.

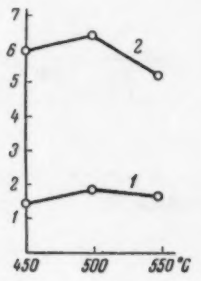

Fig. 2

Fig. 2. Ratio of the yield of phenol over promoted catalysts to that over unpromoted catalysts: 1) over silica gel; 2) over phosphate in the range 450-550°.

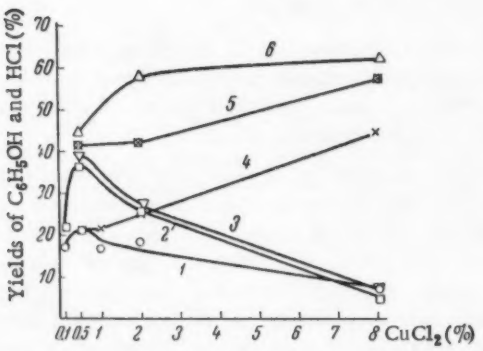

Fig. 3. Effect of cupric chloride content on the hydrolysis of chlorobenzene at various temperatures: 1) 450°, C_6H_5OH; 2) 500°, C_6H_5OH; 3) 550°, C_6H_5OH; 4) 450°, HCl; 5) 500°, HCl; 6) 550°, HCl.

Hence, excess of cupric chloride leads to a sharp reduction in the activity and specificity of the catalyst. The higher the temperature at which the reaction is carried out, the greater is the deactivating effect of excess of cupric acid.

It was established previously that addition of cupric chloride to silica gel that has been deactivated by mineral impurities gives it the high activity that is characteristic of unpoisoned silica gel promoted with cupric chloride [3]. We later found the explanation of this phenomenon. The active centers functioning in promoted silica gel are found mainly in the wider pores, so that blocking of the micropores with mineral impurities does not affect the activity of the catalyst. It is evident that the "regenerating" effect of cupric chloride lies in the transfer of reaction from the fine pores, which are blocked with mineral impurities, to the more accessible part of the surface [4].

Calcium phosphate is nonporous. It would be expected that the addition of cupric chloride to phosphate deactivated with mineral impurity would not give a great "regenerating" effect. This view was confirmed. Table 2 gives the results of experiments with two samples of phosphate catalyst, one of which was deactivated with 8% of sodium chloride and the other was deactivated with 36% of lead acetate [1]. Table 2 shows that the

activity of these catalysts in experiments at 500° increases very little after the addition of 0.5% of cupric chloride: the yields of phenol increased from 0.4 and 0.5 to 2.5 and 4.3%. With phosphate promoted with cupric chloride and not poisoned with mineral impurity the yield of phenol under these conditions was 38%.

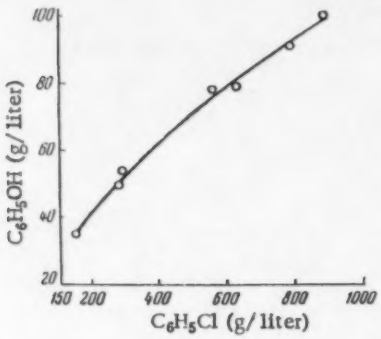

Fig. 4. Relation of productivity of the catalyst to the space velocity of passage of chlorobenzene.

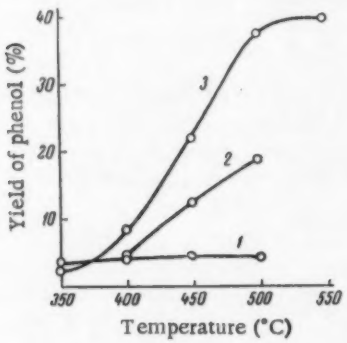

Fig. 5. Comparative reactivities of halobenzenes in their vapor-phase hydrolysis over a phosphate catalyst promoted with cupric chloride: 1) C_6H_5I; 2) C_6H_5Br; 3) C_6H_5Cl.

With increase in the space velocity of passage of chlorobenzene over silica gel promoted with cupric chloride the extent of its conversion diminishes more slowly than the space velocity increases [5]. As Table 3 shows, a similar relation is observed for a phosphate catalyst promoted with cupric chloride. Thus, a sixfold increase in the space velocity of passage of chlorobenzene results in a reduction in the yield of phenol by only one-half (Experiments 1 and 7). Hence, increase in space velocity results in increase in the productivity of the catalyst (Fig. 4).

Hydrolysis of Iodo- and Bromo-benzenes. Results of experiments on the vapor-phase hydrolysis of bromobenzene are given in Table 4 and Fig. 5. In the tables the space velocities of iodo- and bromo-benzenes are given in moles per liter of catalyst per hour. For comparison experiments were carried out also with chlorobenzene. It will be seen from Table 4 that at all temperatures the extent of conversion of bromobenzene into phenol is appreciably lower than that of chlorobenzene. Results of experiments on the hydrolysis of iodobenzene are given in Table 5 and Fig. 5. Since the hydrolysis of iodobenzene is complicated by a side reaction in which free iodine is formed, in the determination of phenol a correction was made, as in [6], for the iodine contained in the reaction products. It will be seen from Table 5 and Fig. 5 that in the hydrolysis of iodobenzene the yield of phenol does not exceed 4.8% and scarcely increases at all with rise in temperature.

The results show that, in the investigated reaction over a phosphate catalyst, the reactivities of halobenzenes diminish in the same order as in the case of silica gel [6]: $C_6H_5Cl > C_6H_5Br > C_6H_5I$.

Ratio of Total and Active Surfaces in Silica Gel and Phosphate Catalysts for the Vapor-phase Hydrolysis of Chlorobenzene. Our comparative investigation of the vapor-phase hydrolysis of chlorobenzene over silica gel and phosphate catalysts under similar conditions makes it possible for us to discuss the question of the ratio of total and active surfaces in them. The specific surface of silica gel attains 500 sq. m/g or more. The specific surface of nonporous calcium phosphate powder is the sum of the geometric surfaces of its crystal faces and does not exceed 3-8 sq. m/g [7]. Thus, the specific surface of the phosphate catalyst is about one-hundredth of the specific surface of silica gel. In view of the fact that these two types of catalysts differ in structure and have widely differing specific surfaces, it would be expected that they would differ also in their behavior in promoting and poisoning. This view was confirmed.

As we showed previously, a silica gel catalyst is exceptionally sensitive to the action of mineral impurities. Only one percent of a sodium, lithium, lead, or zinc salt is sufficient to deactivate unpromoted silica gel almost completely [8]. These small amounts of salts are unable to cover the whole of the enormous surface of silica gel; hence they are adsorbed mainly on its active centers. It is probable that cupric chloride also is adsorbed mainly at active sites, for very small amounts (0.2-0.02%) suffice for optimum promoting of silica gel [9]. Increase in

TABLE 4

Hydrolysis of Bromobenzene over a Phosphate Catalyst Promoted with Cupric Chloride (0.5%)

Experiment	Halobenzene	Temperature (°C)	Space velocity	H_2O / C_6H_5X* (moles)	Yield (%) C_6H_5OH	Yield (%) HX*
1	C_6H_5Cl	400	2.7	5.9	6.3	6.8
2	C_6H_5Br	400	2.2	7.6	4.5	6.2
3	C_6H_5Br	400	2.7	7.3	3.7	5.8
	Regeneration					
4	C_6H_5Cl	450	1.9	7.6	21.5	25.6
5	C_6H_5Br	450	2.3	6.2	12.6	15.9
6	C_6H_5Br	450	2.5	6.7	10.5	13.8
	Regeneration					
7	C_6C_5Cl	500	2.7	6.3	30.1	34.8
8	C_6C_5Br	500	2.6	6.2	18.9	22.6
9	C_6C_5Br	500	2.7	6.2	17.0	20.9

* X is Cl or Br.

TABLE 5

Hydrolysis of Iodobenzene over a Phosphate Catalyst Promoted with Cupric Chloride (0.5%)

Experiment	Temperature (°C)	Space velocity	$\frac{H_2O}{C_6H_5I}$	Yield (%) C_6H_5OH	Yield (%) HI
1	350	2.4	7.6	3.4	0.5
2	350	2.5	9.0	3.1	0.3
3	400	2.3	10.7	3.7	1.2
	Regeneration				
4	450	3.1	6.6	4.6	3.3
5	450	2.5	7.6	4.8	2.3
6	500	3.1	5.9	4.3	6.8
7	500	2.7	6.2	2.4	6.0

the cupric chloride content of the catalyst from 0.2 to 40% by weight has no effect on catalyst activity. The excess of cupric chloride is probably distributed on the inactive part of the silica gel surface. On a phosphate catalyst, cupric chloride is again mainly adsorbed at active sites, for its optimum concentration in the catalyst is small (about 0.5%). Any excess of cupric chloride begins to block the active surface and therefore greatly reduces its activity. Mineral impurities are adsorbed mainly on the inactive part of the phosphate catalyst, since 1-2% of the same lead and sodium salts has a scarcely appreciable effect on catalyst activity [1].

Let us try to make a very rough estimation of the number of active centers in 1 g of phosphate catalyst; this can be calculated from the optimum amount of the copper salt promotor on the assumption that, on the average, every copper atom is associated with one active site. Let us denote the amount (g) of copper salt promotor by a, the weight (g) of phosphate being promoted by m, and Avogadro's number by N. The number of copper atoms, i. e. the number of active centers, in 1 g of phosphate catalyst will be $A = \frac{a \cdot N}{m \cdot 234}$.

In our experiments 234 is the molecular weight of cupric chloride (dihydrate), a is 0.25, and m is 50; hence $A = 1.3 \cdot 10^{19}$. The similarity in catalytic activity between silica gel and phosphate despite great difference in specific surface enables us to assume that the concentration of active sites on the surface of silica gel

(regarded as homogeneous) will be approximately one-hundredth of that on the surface of phosphate, i. e. of the order of 10^{17}.

The orders of magnitude of numbers of active centers in unit masses (1 g) of other types of catalysts of high specific surface were determined by Dohse [10] for the dehydration of alcohol over bauxite ($2\text{-}3 \cdot 10^{19}$), by Balandin and Vasserberg [11] for the same reaction over Al_2O_3-ZnO ($1.7 \cdot 10^{19}$), by Sokol'skii [12] for the hydrogenation of cinnamic acid over Raney nickel (10^{20}), and by Freidlin and Levit [13] for the dehydration of formic acid ($1.7 \cdot 10^{20}$) and of ethanol ($1.7 \cdot 10^{20}$) over silica gel.

SUMMARY

1. The vapor-phase hydrolysis of halobenzenes over a phosphate catalyst promoted with cupric chloride was investigated.

2. It was shown that, as in the presence of silica gel, in the presence of tricalcium phosphate the hydrolysis of chlorobenzene is promoted by cupric chloride.

3. It was found that the reactivities of halobenzenes in the investigated reaction fall in the same order as in presence of silica gel.

4. The question of the ratio between total and active surface in silica gel and phosphate catalysts was discussed. The number of active sites in the catalyst was estimated.

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SYNTHESIS OF α-HALO CARBOXYLIC ACIDS CONTAINING ACTIVE GROUPS IN THE ω-POSITION

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As we showed previously [1, 2], α-chloro acids can readily be prepared by the action of chlorine in a sulfuric acid medium on compounds containing a $CCl_2=CH$ group:

$$R-CH=CCl_2+Cl_2+H_2SO_4 \rightarrow [RCHClCCl_2 \cdot OSO_3H] \xrightarrow{H_2O} RCHClCOOH.$$

A similar reaction proceeds also in a medium of perchloric acid, but in several cases that have been studied it does not go in phosphoric and acetic acids [2]. Consequently, the application of the method to compounds containing groups that are unstable in strong acids, e. g. CN and COOR, has been limited.

It is known that the yields of β-halo esters obtained by the action of halogen on olefins in carboxylic acid media can be raised by the addition of mercury salts to the reaction mixture [3]. In the present investigation we have succeeded in obtaining α-halo acids by the action of chlorine or bromine on compounds containing the $CCl_2=CH$ group in an acetic acid medium in presence of mercuric acetate:

$$R-CH=CCl_2+Cl_2+CH_3COOH \xrightarrow{Hg(OCOCH_3)_2} [RCHClCCl_2 \cdot OCOCH_3] \xrightarrow{H_2O} RCHClCOOH.$$

In this way we prepared 2-bromo-5-chloro-, 2,5-dichloro-, 5-acetoxy-2-chloro-, and 2-chloro-5-cyanovaleric acids from 1,1,5-trichloro-, 5-acetoxy-1,1-dichloro-, and 1,1-dichloro-5-cyano-1-pentenes, and 2-chloro-3-methoxy- and 3-acetoxy-2-chloro-propionic acids from 1,1-dichloro-3-methoxy- and 3-acetoxy-1,1-dichloro-propenes. Under these conditions we succeeded also in preparing α-chlorohydrocinnamic acid from 1,1-dichloro-3-phenylpropene.* The yields of α-chloro acids were 50-60%. In the case of 2-chloro-3-methoxy- and 3-acetoxy-2-chloro-propionic acids the yields were only 25 and 27%, respectively. The yield of α-bromo acid was also low, though in this case 40% of the trichloropropene was recovered unchanged.

In general, there is no satisfactory method of preparing α,α-dichloro acids. These acids are generally prepared from α-keto acids or, in the case of perchloro compounds, by the oxidation of unsaturated compounds. By the action of chlorine on 1,1,2,5-tetrachloro-1-pentene in acetic acid in presence of mercuric acetate we obtained a compound corresponding in analysis to the expected 2,2,5-trichlorovaleric acid. Hence, in the given conditions, even a trichlorovinyl group, whose double bond is greatly impoverished in electrons, is capable of conjugated addition of chlorine and acetic acid. In all cases products formed by the addition of halogen at the double bond were isolated as well as the acids.

EXPERIMENTAL

Preparation of 2,5-Dichlorovaleric Acid from 1,1,5-Trichloro-1-Pentene. Chlorine was passed through a mixture of 63.6 g of mercuric acetate, 34.7 g of 1,1,5-trichloro-1-pentene, and 100 ml of glacial acetic acid until decolorization was complete. The precipitate was filtered off, and acetic acid was distilled from the filtrate. The residue was dissolved in chloroform, and the solution was washed with a little dilute hydrochloric acid. The acidic products were extracted from the chloroform solution with concentrated sodium carbonate

* When the reaction between this dichlorophenylpropene and chlorine is carried out in a medium of concentrated sulfuric acid, a more highly chlorinated acid is formed.

solution. Acidification of the alkaline extracts gave 2,5-dichlorovaleric acid; the yield of the acid was 21 g (62%) and it had b.p. 107° (1 mm); n_D^{20} 1.4860; d_4^{20} 1.3480; found MR 36.45; calculated MR 36.56. For 2,5-dichlorovaleric acid the literature [1] gives b.p. 106-107° (1 mm); n_D^{20} 1.4825; d_4^{20} 1.3421 [1].

We obtained also 16.4 g of neutral products, namely 2 g of unchanged trichloropentene and 14.4 g of 1,1,1,2,5-pentachloropentane, b. p. 86-87° (2 mm); n_D^{20} 1.5095; d_4^{20} 1.4798; found MR 49.38; calculated MR 49.62. The literature [1] gives b. p. 86-87° (2 mm); n_D^{20} 1.5100; d_4^{20} 1.4806 [1].

Preparation of 5-Acetoxy-2-chlorovaleric Acid from 5-Acetoxy-1,1-dichloro-1-pentene. The reaction and the treatment of the reaction mixture were carried out as in the preceding experiment: passage of chlorine through a mixture of 39.4 g of the acetoxydichloropentene, 63.6 g of mercuric acetate, and 100 ml of glacial acetic acid gave 21.5 g (55%) of 5-acetoxy-2-chlorovaleric acid, b. p. 126-127° (1 mm); n_D^{20} 1.4640; d_4^{20} 1.2633; found MR 42.51; calculated MR 42.58

Found %: Cl 18.26; 18.36
$C_7H_{10}ClO_4$. Calculated %: Cl 18.22

Its acid chloride had b.p. 133° (18 mm); n_D^{20} 1.4668; d_4^{20} 1.2765; found MR 46.30; calculated MR 46.29.

We obtained also 22 g of neutral products, namely 3.2 g of unchanged acetoxydichloropentene and 18.8 g (35%) of 5-acetoxy-1,1,1,2-tetrachloropentane, b. p. 100-101° (1.5 mm); n_D^{20} 1.4870; d_4^{20} 1.3834; found MR 55.71; calculated MR 55.65

Found %: C 31.19; 31.32, H 3.99; 3.75; Cl 52.43
$C_7H_{10}Cl_4O_2$. Calculated %: C 31.37; H 3.37; Cl 52.93

Preparation of 2-Chloro-5-cyanovaleric Acid from 1,1-Dichloro-5-cyano-1-pentene. Chlorine was passed through a mixture of 32.8 g of 1,1-dichloro-5-cyano-1-pentene, 63.6 g of mercuric acetate, and 100 ml of glacial acetic acid at 50° with stirring until decolorization was complete. The precipitate was filtered off, acetic acid was distilled from the filtrate, and the residue was dissolved in ether. The precipitate of mercury salt that then formed was filtered off. Acidic products were extracted from the ethereal solution with concentrated sodium carbonate solution, and the extract was acidified and repeatedly extracted with ether; the ether extract was dried over calcium chloride. Distillation gave 17.4 g (54%) of 2-chloro-5-cyanovaleric acid, b. p. 150° (1 mm); [162° (3 mm)]; n_D^{20} 1.4770; d_4^{20} 1.2660; found MR 36.06; calculated MR 36.13

Found %: C 44.47; 44.27; H 5.09; 5.05; Cl 22.24
$C_6H_8NClO_2$. Calculated %: C 44.60; H 4.98; Cl 21.95

Its acid chloride had b.p. 110° (2 mm); n_D^{20} 1.4830; d_4^{20} 1.3072; found MR 39.33; calculated MR 39.47 [4].

Hydrolysis with sulfuric acid gave 2-chlorohexanedioic acid, m. p. 102°, alone and in admixture with known 2-chlorohexanedioic acid.

We obtained also 16.5 g of neutral products, namely, 2.5 g of unchanged 1,1-dichloro-5-cyano-1-pentene and 14 g (30%) of 1,1,1,2-tetrachloro-5-cyanopentane, b. p. 116° (2 mm); n_D^{20} 1.5045; d_4^{20} 1.4087; found MR 49.43; calculated MR 49.19

Found %: C 31.09; 31.04; H 3.03; 3.17
$C_6H_7NCl_4$. Calculated %: C 30.67; H 3.00

Preparation of 3-Acetoxy-2-chloropropionic Acid from 3-Acetoxy-1,1-dichloropropene. The reaction and the treatment of the products were carried out as in the preceding experiment: passage of chlorine through a mixture of 33.8 g of 3-acetoxy-1,1-dichloropropene, 63.6 g of mercuric acetate, and 100 ml of glacial acetic acid at 40° gave 9 g (27.1%) of 3-acetoxy-2-chloropropionic acid, b. p. 112° (1.5 mm); n_D^{20} 1.4570; d_4^{20} 1.3496; found MR 33.61; calculated MR 33.34

Found %: C 36.24; 36.22; H 4.40; 4.33
$C_5H_7ClO_4$. Calculated %: C 36.06; H 4.24

Its acid chloride had b.p. 90-91° (17 mm); n_D^{20} 1.4565; d_4^{20} 1.3671; found MR 36.82; calculated MR 37.05.

We obtained also 29.4 g of neutral products, namely, 3 g of unchanged 3-acetoxy-1,1-dichloropropene and 26.4 g (55%) of 3-acetoxy-1,1,1,2-tetrachloropropane, b.p. 117-118° (24 mm); n_D^{20} 1.4860; d_4^{20} 1.4899; found MR 36.75; calculated MR 36.41. The literature [2] gives b.p. 81-82° (2 mm); n_D^{20} 1.4858; d_4^{20} 1.4905

Preparation of 2-Chloro-3-methoxypropionic Acid from 1,1-Dichloro-3-methoxypropene. The reaction was carried out as in the preceding experiment: passage of chlorine through a mixture of 28.2 g of 1,1-dichloro-3-methoxypropene, 63.6 g of mercuric acetate, and 100 ml of glacial acetic acid at 30° gave 7 g (25.2%) of 2-chloro-3-methoxypropionic acid, b.p. 79° (1.5 mm); n_D^{20} 1.4569; d_4^{20} 1.3216; found MR 28.55; calculated MR 28.72

Found %: C 34.80; 34.65; H 4.99; 4.98
$C_4H_7ClO_3$. Calculated %: C 34.67; H 5.09

Its acid chloride had b.p. 63-65° (24 mm); n_D^{20} 1.4590; d_4^{20} 1.3216; found MR 32.51; calculated MR 32.82.

We obtained also 24.6 g of neutral products, of which 4 g was unchanged dichloromethoxypropene. We were unable to isolate any individual substances from the residue.

Preparation of α-Chlorohydrocinnamic Acid from 1,1-Dichloro-3-phenylpropene. The reaction was carried out as in the preceding experiment: passage of chlorine through a mixture of 56.1 g of 1,1-dichloro-3-phenylpropene, 95.4 g of mercuric acetate, and 150 ml of acetic acid at 55-60° gave 25 g (45.3% on the dichloro-phenylpropene taken for reaction and 54% on that which reacted) of α-chlorohydrocinnamic acid, b.p. 132° (2 mm), m.p. 51° (from heptane).

Found %: C 58.53; 58.52; H 4.79; 4.96
$C_9H_9ClO_2$. Calculated %: C 58.55; H 4.92

Its acid chloride had b.p. 74° (2 mm); n_D^{20} 1.5430; d_4^{20} 1.2647; found MR 50.68; calculated MR 50.64.

Its amide had m.p. 93° (from water); the literature [4] gives 95°.

Found %: C 58.48; 58.50; H 5.38; 5.25; Cl 19.42; 19.13
$C_9H_{12}NClO$. Calculated %: C 58.86; H 5.49; Cl 19.31

Its anilide had m.p. 125° (from water-alcohol).

Found %: N 5.02; 5.05
$C_{15}H_{14}NClO$. Calculated %: N 5.01

Its ethyl ester had b.p. 110° (8 mm); n_D^{20} 1.5092; d_4^{20} 1.1312; found MR 55.76; calculated MR 55.92

Found %: C 61.52; 61.54; H 6.03; 6.14
$C_{11}H_{13}ClO_2$. Calculated %: C 62.10; H 6.16

Dehydrochlorination of the acid with alcoholic alkali gave cinnamic acid, m.p. 129°, alone and in admixture with known cinnamic acid.

We obtained also 37.5 g of neutral products, namely, 9 g of unchanged 1,1-dichloro-3-phenylpropene and 28.5 g (37%) of 1,1,1,2-tetrachloro-3-phenylpropane, b.p. 122° (3 mm); n_D^{20} 1.5555; d_4^{20} 1.3875; found MR 59.72; calculated MR 59.63. The literature [5] gives b.p. 111-112° (2 mm); n_D^{20} 1.5535; d_4^{20} 1.3867.

Addition of Chlorine to 1,1,2,5-tetrachloro-1-pentene in an Acetic Acid Medium. The procedure was similar to that of the preceding experiment. Passage of chlorine through a mixture of 41.6 g of 1,1,2,5-tetrachloro-1-pentene, 63.6 g of mercuric acetate, and 100 ml of glacial acetic acid at 70° gave 8 g (19.5% on the tetrachloropentene taken and 25% on that which reacted) of an acid that was evidently 2,2,5-trichlorovaleric acid, b.p. 117° (2 mm); n_D^{20} 1.4950; d_4^{20} 1.4475; found MR 41.40; calculated MR 41.35

Found %: C 28.96; 29.18; H 3.52; 3.60; Cl 51.12; 51.18
$C_5H_7Cl_3O_2$. Calculated %: C 29.22; H 3.44; Cl 51.77

We obtained also 36.5 g of neutral products, namely, 9.1 g of unchanged tetrachloropentene and 27.4 g (48.9%) of 1,1,1,2,2,5-hexachloropentane, b. p. 93° (2 mm); n_D^{20} 1.5260; d_4^{20} 1.5896; found MR 54.04; calculated MR 54.49

Found %: C 21.69; 21.71; H 2.29; 2.34; Cl 75.49
$C_5H_6Cl_6$. Calculated %: C 21.54; H 2.15; Cl 76.30

Preparation of 2-Bromo-3-chlorovaleric Acid from 1,1,5-Trichloro-1-pentene. 1,1,5-Trichloro-1-pentene (34.7 g) was added gradually to a stirred mixture of 63.6 g of mercuric acetate, 100 ml of glacial acetic acid, and 64 g of bromine. Reaction was accompanied by evolution of heat. When the mixture was cool, the precipitate was filtered off, acetic acid was distilled from the filtrate, the residue was dissolved in chloroform, and the solution was washed free from mercury salts with dilute hydrochloric acid. Acidic products were extracted from the chloroform solution with concentrated sodium carbonate solution. After acidification of the alkaline extract and the usual purification of the product, we isolated 10.5 g (24.4% on the trichloropentene taken and 48% on that which reacted) of 2-bromo-3-chlorovaleric acid, b.p. 106-107° (0.5 mm); n_D^{20} 1.5070; d_4^{20} 1.6215; found MR 39.54; calculated MR 39.46. The literature [6] gives b.p. 126-127° (2.5 mm); n_D^{20} 1.5068; d_4^{20} 1.6307.

We obtained also 35.7 g of neutral products, namely, 14 g of unchanged trichloropentene and 21.7 g of 1,2-dibromo-1,1,5-trichloropentane, b. p. 84-85° (1 mm); n_D^{20} 1.5562; d_4^{20} 1.9322; found MR 55.46; calculated MR 55.42.

SUMMARY

1. It was found that compounds of the type $CCl_2 = CX(CH_2)_nY$ (X = H or Hal; Y = various groups) react with halogen in acetic acid in presence of mercuric acetate with formation (after treatment with water) of α-halo or α,α-dihalo carboxylic acids.

2. In this way the following acids were prepared: $Cl(CH_2)_3CHClCOOH$; $Cl(CH_2)_3CHBrCOOH$; $CH_3COO(CH_2)_3CHClCOOH$; $CN(CH_2)_3CHClCOOH$; $CH_3COOCH_2CHClCOOH$; $CH_3OCH_2CHClCOOH$; $C_6H_5CH_2CHClCOOH$; $Cl(CH_2)_3CCl_2COOH$.

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CHANGES IN THE CATALYTIC ACTIVITY OF SILICON-COPPER ALLOYS IN THE COURSE OF THE DIRECT SYNTHESIS OF CHLOROETHYLSILANES

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The direct synthesis of alkyl- and aryl-chlorosilanes by the action of halogen derivatives on silicon in presence of a catalyst (copper) has been the subject of several investigations [1], which have been concerned mainly with the preparation of chloromethylsilanes. In the published investigations, reactions of this type have been evaluated not in terms of their course and kinetics, but in terms of the total yield and average composition of products obtained finally as a result of prolonged reaction. There are only isolated references to the fact that in the course of the synthesis the activity of the silicon-copper catalyst gradually falls (it is supposed that this occurs as a result of the deposition of carbon in the mass) [2], but no systematic investigation of changes in activity during reaction has been carried out. However, as reaction between silicon and alkyl halide proceeds, the composition and structure of the catalyst changes greatly. As we showed previously [3], this must have an effect on the activity of the catalyst. In the present investigation we attempted to follow the changes in the catalytic activity of silicon-copper alloys in the course of the synthesis and to elucidate the causes of these changes, taking the reaction with ethyl chloride as our example.

The synthesis of chloroethylsilanes was carried out in a "fluid bed" by the procedure that we developed previously [4], and as measures of the changes occurring we chose the total activity of the alloy, defined as the quantitative yield of chloroethylsilanes per hour per 100 g of catalyst (productivity), and the selectivity of the catalyst in the most favored reaction (formation of the main reaction product, dichlorodiethylsilane):

$$2C_2H_5Cl + Si \rightarrow (C_2H_5)_2SiCl_2.$$

The selectivity of the catalyst was measured by the dichlorodiethylsilane content of the mixture of chloroethylsilanes formed in the reaction. Figure 1 shows the results of the activity investigation for silicon-copper alloys containing 5-9% of copper. In all experiments there was a sharp change in activity in the course of the synthesis; moreover, both the curves for dichlorodiethylsilane content against time and the curves for yield of mixture of chloroethylsilanes against time passed through two well defined maxima having identical positions on the time scale on both curves. The first activity maximum is observed during the first hour of reaction, and the second is observed after 7-12 hours. The activity of the mass falls after 15-25 hours of work.

Figure 2 presents results of an investigation by an analogous method on two alloys of higher copper content (about 25%). In these experiments the activity curves have one maximum each, the maximum on the selectivity curve being at 1-2 hours from the start of reaction and the maximum on the curve for total activity (productivity) being at about four hours from the start of reaction. The fall in activity in the further course of the process was much more rapid, and already after 7-11 hours the synthesis practically came to a stop.

As indicated above, as one of the possible causes of the fall in catalytic activity the literature refers to poisoning with carbon, which is formed in the synthesis in appreciable amounts (in our experiments, about 10% in the spent catalyst). In order to verify this suggestion we carried out a series of experiments in which carbon was introduced by the decomposition of sugar on the fresh silicon-copper alloy. The results of the experiments (Table 6) showed that the introduction of carbon results in some reduction in the total activity (productivity) of

the silicon-copper alloy, but the dichlorodiethylsilane content of the reaction products is not appreciably affected.

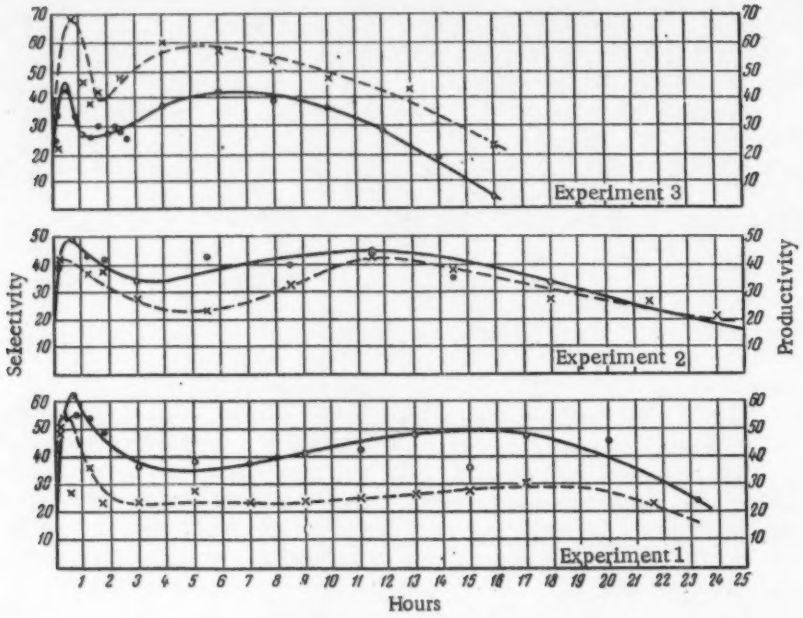

Fig. 1. Changes in the activities of alloys containing 5-9% of copper during the synthesis: – – –) change in total activity (productivity) (grams of mixture of chloroethylsilanes per 100 g of catalyst mass per hour); ———) change in selectivity (% content of dichlorodiethylsilane in mixture of chloroethylsilanes).

The lowering of the activity of the carbonized alloy could be explained by the action of the carbon deposit in hindering the access of ethyl chloride to the surface. This view is not confirmed by our experiments on the liberation of hydrogen when the alloy is treated with alkali (Table 7, Experiments 1-4). Both fresh alloys and fresh alloys that have been carbonized yield hydrogen at approximately the same rate. Hence, the lowering of total activity (productivity) of silicon-copper alloys during the synthesis is associated only partially with the deposition of carbon, which probably occurs on active places on the copper. The almost total cessation of reaction in the final stage of the process, when the silicon content of the catalyst mass is still high (in some cases 40-55%), cannot be explained solely by the accumulation of carbon.

On the basis of microscopic studies of the structure of alloys it was suggested [5] that the lowering of the efficiency of the silicon catalyst in the reaction with ethyl chloride is associated with the separation of copper on the surface of the particles of the spent mass. In order to determine the extent to which the separated copper hinders chemical reactions of the silicon, we carried out experiments on the leaching of spent alloys (Experiments 5 and 6; Table 7). The rate of liberation of hydrogen in reaction with alkali was found to be several times as great for fresh alloys and for carbonized fresh alloys as for spent alloys containing the same amount of silicon. Hence, experiment is in accord with the view that copper screens the silicon surface in spent alloys.

In all probability, the great lowering in the activity of the catalyst mass at the end of the synthesis is to be explained by the separation of considerable amounts of copper during the synthesis, its distribution over the surface of the silicon, and the consequent reduction in the efficiency of contact with ethyl chloride. This view is confirmed also by the fact that alloys of low copper content preserve their activity for a long time (15-25 hours with a yield of 330-383 g of the mixture of chloroethylsilanes per 100 g of alloy taken in the experiment), whereas alloys of high copper content rapidly lose their activity (7-11 hours with a yield of 100-171 g of the mixture of chloroethylsilanes per 100 g of alloy).

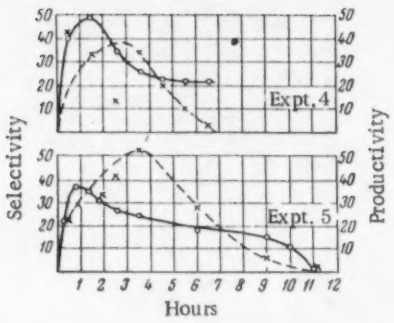

Fig. 2. Changes in the activities of alloys containing 24.7-25.8% of copper during the synthesis: – – –) change in total activity (productivity) (grams of mixture of chloroethylsilanes per 100 g of catalyst mass per hour); ———) change in selectivity (% content of dichlorodiethylsilane in mixture of chloroethylsilanes).

As x-ray analysis has shown [5], the silicon-copper alloys that we used contain silicon and the intermetallic compound Cu_3Si, in which the whole of the copper present is combined. Reaction of ethyl chloride with the silicon combined in the intermetallic compound results in the breakdown of this compound with formation of copper, which is a catalyst for the subsequent reaction of ethyl chloride with silicon. The attainment of the maximum activity of the catalyst mass is probably associated with the accumulation of the optimum amount of catalyst (copper) formed by the decomposition of the intermetallic compound.

In accordance with this discussion and with the results of our investigation, we consider it possible to advance the following hypotheses concerning the causes of the change in activity of alloys during the synthesis of chloroethylsilanes and concerning the above-mentioned differences in the course of reaction for alloys of low copper content (5-9%) and alloys of high copper content (25%). In the interaction of ethyl chloride with silicon-copper alloy both reaction with silicon of the intermetallic compound (substantially complete in the first few hours of the work of the catalyst mass) and also simultaneous reaction with free silicon under the catalytic action of copper (which separates in the breakdown of the intermetallic compound Cu_3Si) occur. Whereas in the first hours of the synthesis reaction of the first type predominates, in the subsequent hours, as the intermetallic compound breaks down and active copper accumulates, the second process begins to assume the principal part.

For alloys of low copper content the course of the curve for the change of activity with time can be explained on the hypothesis that the accumulation of the optimum amount of catalyst (active copper) occupies a long time owing to the low concentration of the intermetallic compound Cu_3Si in the original alloy (7-12 hours from the start of the synthesis; the second maximum on the curves of Fig. 1). The first maximum of the curves corresponds to maximum rate of breakdown of the intermetallic compound. Later, the rate of this process falls as a result of reduction in the concentration of the intermetallic compound and, possibly, as a result of partial blocking of its surface by the copper liberated in the breakdown. At this point the amount of copper liberated has still not attained the optimum value, so that the maximum is followed by a fall in the activity of the mass and then, as the copper accumulates and approaches its optimum amount, by a new rise.

A different picture is observed for alloys of high copper content, in which the concentration of the intermetallic compound Cu_3Si is correspondingly higher. The optimum amount of copper necessary for the attainment of the highest content of dichlorodiethylsilane in the mixture of chloroethylsilanes is liberated during the first 1-2 hours of the synthesis, i.e., considerably more rapidly than in alloys of low copper content. Further breakdown of the intermetallic compound with separation of further amounts of copper will favor increase in productivity with lowering of the selectivity of the catalyst mass (lowering of the dichlorodiethylsilane content). This is fully in accord with previously published data [3], which shows that increase in the copper content of alloys above the optimum value results in increase in the extent to which side reactions occur and reduction in the selectivity of the catalyst mass. Accordingly, the curves in Fig. 2 have only one maximum each, and the maximum dichlorodiethylsilane content is attained after the first 1-2 hours of reaction, whereas maximum total activity is attained only after 3-4 hours, when the considerable amount of copper accumulated no longer corresponds to optimum selectivity of the catalyst mass for the formation of dichlorodiethylsilane.

There follows a general fall in the activity of the catalyst mass associated with the removal of silicon and the accumulation of copper in amounts considerably exceeding the optimum amount. This results in intensification of breakdown processes, lowering of the content of dichlorodiethylsilane, increase in the deposition of carbon on active centers of the catalyst mass, and therefore to a sharp fall in total activity.

TABLE 1

Change in the Activity of the Alloy in Experiment 1

	Test No.															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
From start of test	0 hr. 17 min	0 hr. 30 min.	0 hr. 45 min.	1 hr. 00 min.	1 hr. 30 min.	2 hr. 00 min.	4 hr. 00 min.	6 hr. 00 min.	8 hr. 00 min.	10 hr. 00 min.	12 hr. 00 min.	14 hr. 00 min.	16 hr. 00 min.	18 hr. 00 min.	22 hr. 00 min.	24 hr. 30 min.
Amt. mixture of chloroethylsilanes obtained (g)	55.6	43.3	26.0	31.0	60.6	40.3	163	155	123	125.0	110.2	96.0	90.0	84.2	70.2	82.0
Composition of mixture (%):																
dichloroethylsilane	16.2	18.4	9.6	15.3	17.7	15.7	21.6	18.9	21.7	17.6	15.6	11.5	30.5	11.9	8.3	29.1
trichloroethylsilane*	29.7	20.7	17.4	20.5	18.7	25.6	32.1	32.4	30.2	31.4	31.2	29.8	24.0	40.1	37.0	37.3
dichlorodiethylsilane	44.2	51.0	63.0	54.2	53.5	48.8	36.3	38.8	38.1	41.0	43.2	48.8	35.6	48.0	44.6	23.6
residue in still	9.9	9.9	10.0	10.0	10.1	9.9	10.0	9.9	10.0	10.0	10.0	9.9	9.9		10.1	10.0
Productivity	49.6	52.3	27.9	33.9	34.1	23.6	23.8	27.3	24.0	24.5	24.3	27.0	28.6	30.5	14.7***	32.8***

* Chlorodiethylsilane impurity is present.

** In grams of mixture of chloroethylsilanes per 100 g of mass per hour.

*** In the construction of the graphical representation the mean of two tests was taken.

TABLE 2

Change in the Activity of the Alloy in Experiment 2

	Test No.											
	1	2	3	4	5	6	7	8	9	10	11	12
From start of test	0 hr. 30 min.	0 hr. 45 min.	1 hr. 30 min.	2 hr. 00 min.	4 hr. 00 min.	7 hr. 00 min.	10 hr. 00 min.	13 hr. 00 min.	16 hr. 00 min.	20 hr. 00 min.	23 hr. 00 min.	25 hr. 00 min.
Amt. mixture of chloroethylsilanes obtained (g)	79.7	36.7	95.0	63.3	159.3	177.5	189.3	201	133	103.2	56.9	24.3
Composition of mixture (%)												
dichloroethylsilane	25.3	21.1	17.7	22.7	29.7	23.5	19.8	19.5	27.6	29.3	37.0	41.1
trichloroethylsilane*	25.3	19.0	29.5	26.1	26.9	24.2	30.6	26.3	26.5	27.9	28.5	39.4
dichlorodiethylsilane	39.3	49.8	42.8	41.0	33.5	42.3	39.7	44.2	35.9	32.8	24.5	19.5
residue in still	10.1	10.1	10.0	10.2	9.9	10.0	9.9	10.0	10.0	10.0	10.0	
Productivity	41.3	40.3	36.7	38.6	26.8	23.6	31.0	42.7	37.3	28.0	26.1	19.5

* Chlorodiethylsilane impurity is present.

TABLE 3

Change in the Activity of the Alloy in Experiment 3

	Test No.															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
From start of test	0 hr. 25 min.	0 hr. 45 min.	1 hr. 02 min.	1 hr. 17 min.	1 hr. 37 min.	1 hr. 57 min.	2 hr. 22 min.	2 hr. 40 min.	3 hr. 00 min.	5 hr. 00 min.	7hr. 00 min.	9 hr. 00 min.	11 hr. 00 min.	13 hr. 00 min.	15 hr. 00 min.	17 hr. 00 min.
Amt. mixture of chloroethylsilanes obtained (g)	35.7	53.3	71.7	41.1	44.9	46.2	58.1	64.2	29.9	315	227	188	133	75.5	109	37.5
Composition of mixture (%)																
dichloroethyl-silane	30.4	21.0	28.1	37.1	35.1	27.2	30.7	30.4	37.4	27.6	20.2	26.6	22.5	31.7	42.1	64.7
trichloroethyl-silane*	26.5	23.3	28.9	26.7	29.1	32.1	29.5	32.0	28.6	26.2	28.4	25.0	31.0	29.7	28.9	25.5
dichlorodiethyl-silane	33.0	45.7	33.0	26.3	25.8	30.7	29.8	27.6	24.0	36.2	41.3	38.5	36.5	28.7	18.9	4.1
Residue in still	10.1	10.0	10.0	9.9	10.0	10.0	10.0	10.0	10.0	10.0	10.1	9.9	10.0	9.9	10.1	5.7
Productivity	21.6	41.4	67.7	45.5	38.6	41.0	42.8**	68.7**	29.2**	60.3	56.2	52.5	46.4	31.5***	55.7***	23.4

* Chlorodiethylsilane impurity is present.

** In the construction of the graphical representation the mean of three tests was taken.

*** In the construction of the graphical representation the mean of two tests was taken.

EXPERIMENTAL

Change in the Activities of Alloys during the Synthesis. The starting materials for the synthesis of chloroethylsilanes were ethyl chloride and finely ground alloys of copper (M-2 quality) and silicon (Kr-1 quality). The apparatus for the synthesis was described previously [4]. Ethyl chloride was passed through a reactor containing the alloy powder (400 g in each experiment) at 330-360°, and the reaction products condensed and passed to a receiver, which was emptied periodically so that the composition of the product and the productivity of the catalyst mass could be determined. The separation of the mixture of chloroethylsilanes was effected by fractionation through a column of 20 theoretical plates, and the composition was calculated from the results of the separation and analysis of the fractions by the accepted method [4]. In the calculation of the productivity of the catalyst mass at each point of time it was assumed that the amount of catalyst mass in the reactor diminished (from the original weight of alloy to the final weight) in proportion to the amount of chloroethylsilanes obtained since the start of the experiment.

In the initial period of the synthesis (the first two hours), which was characterized by a particularly sharp change in activity, test samples were taken and the composition of the reaction products was determined every 15-30 minutes, but afterwards only every two hours. In Experiment 1 we used an alloy containing 5.2% of copper; in the course of 24 hours 30 minutes we took and analyzed 16 test samples of the reaction products. Owing to the fall in activity, the synthesis was then stopped, and the spent mass (90.7 g) was unloaded and analyzed. The composition of the spent mass was copper 14.2%, silicon 55.5%, and carbon 6.6%. Table 1 gives the results of the separation of the test samples taken during the synthesis, and Fig. 1 gives the curves for change in activity constructed from the data obtained.

In Experiment 2 the copper content of the original alloy was 5.4% and the duration of the experiment was 25 hours. The spent catalyst mass (58.7 g) had the following composition: copper 23.3%, silicon 41.3%, copper 11%. Table 2 gives results of analyses of 12 test samples taken during the synthesis, and Fig. 1 gives the curves for change in activity based on these results. In Experiment 3 (8.6% of copper in the original alloy) 75 g of

TABLE 4

Change in the Activity of the Alloy in Experiment 4

	Test No.						
	1	2	3	4	5	6	7
From start of test	1 hr. 00 min.	2 hr. 00 min.	3 hr. 00 min.	4 hr. 00min.	5 hr. 00 min.	6 hr. 00 min.	7 hr. 00min.
Amt. mixture of chloroethylsilanes obtained (g)	148	86.5	27.8	35.8	33.8	14.9	4.5
Composition of mixture (%):							
dichloroethylsilane	20.9	24.9	30.6	43.4	31.8	43.0	27.7
trichloroethylsilane*	26.2	27.1	25.3	21.9	27.1	26.9	39.2
dichlorodiethylsilane	40.0	48.0	33.0	26.0	23.0	23.0	22.0
residue in still	12.9	—	11.1	8.7	18.1	7.1	11.1
Productivity	42.2	32.1	12.4	36.4	21.0	10.7	3.2

* Chlorodiethylsilane impurity is present.

spent mass (33.1% of copper, 28.9% of silicon, 12.6% of carbon) was unloaded after 17 hours of work. The results of the analysis of 16 test samples taken are given in Table 3 and Fig. 1. In Experiment 4 the copper content of the original alloy was 25.5% and 350 g was taken; after seven hours 136 g of spent mass was unloaded; results of the analysis of seven test samples are given in Table 4 and Fig. 2. In Experiment 5 (24.7% of copper in the original alloy) after 12 hours of work we unloaded 127 g of spent mass (63.6% of copper, 10.6% of silicon, 8.5% of carbon). The results of the analysis of nine test samples are given in Table 5 and Fig. 2.

Experiments on the Introduction of Carbon into the Original Alloy. Finely ground alloy (306 g) was mixed with 140 g of 75% aqueous sugar solution, and the mixture was dried in a drying cupboard, placed in the reactor for the synthesis of chloroethylsilanes, and heated gradually to 400° in a stream of nitrogen. The synthesis of chloroethylsilanes was then carried out over this mass (duration of all experiments 2 hours; amount of mass

TABLE 5

Change in the Activity of the Alloy in Experiment 5

	Test No.								
	1	2	3	4	5	6	7	8	9
From start of test	0 hr. 35 min	1 hr. 00 min	1 hr. 30 min	2 hr. 00 min	3 hr. 00 min	4 hr. 00 min	8 hr. 00 min	10 hr. 00 min	12 hr. 00 min
Amt. mixture of chloroethylsilanes obtained (g)	47.8	43.7	60.2	52.1	126.5	132.6	202	13.6	5.1
Composition of mixture (%)									
dichloroethylsilane	41.5	33.6	26.6	32.6	34.8	35.5	44.0	50.3	56.9
trichloroethylsilane	26.5	20.5	29.6	27.9	29.4	29.7	27.8	29.9	35.3
dichlorodiethylsilane	21.9	35.8	33.8	29.5	25.8	24.8	18.1	14.7	0.0
residue in still	10.1	10.1	10.0	10.0	10.0	10.0	10.1	5.1	7.8
Productivity	21.0	28.1	34.0	31.0	41.8	52.1	27.6	5.1	2.0

TABLE 6

Experiments on the Introduction of Carbon into the Fresh Alloy

Experiment	Original alloy				Chloroethylsilanes obtained (g)		Composition of mixture of chloroethylsilanes (%)			
	Form	Composition (%)			during the expt.	calc. for 100 g of alloy/hr.	dichloroethylsilane	trichloroethylsilane	dichlorodiethylsilane	residue in still
		Si	Cu	C						
1	Fresh	73.4	24.7	0	301	43.0	51.0	22.6	16.4	10.0
2	Carbonized	66.7	22.5	10.0	138	19.7	43.9	27.4	18.6	10.1
3	Fresh	83.0	14.9	0.0	383	54.7	16.3	27.6	46.2	9.9
4	Carbonized	76.0	13.7	8.5	194	27.7	21.9	29.2	38.9	10.0
5	Fresh	73.4	24.7	0.0	141	20.1	40.9	24.3	24.8	10.0
6	After use with $C_2H_5SiHCl_2$	73.4	24.7	—	95	13.5	35.8	26.4	27.7	10.1

TABLE 7

Reaction of Silicon-Copper Alloys with Alkali

Expt.	Description of alloy	Composition (%) according to analysis			Vol. H liberated
		Cu	Si	C	
1	Fresh	24.7	73.4	0.0	2.2
2	Fresh	24.7	73.4	0.0	2.5
3	Fresh	63.2	35.1	0.0	4.6
4	Fresh, carbonized	22.5	66.7	10.0	4.5
5	Spent in Experiment 2 (Table 2)	23.3	41.3	11.0	0.9
6	Spent in Experiment 3 (Table 3)	33.1	28.9	12.6	0.4

taken 350 g). Table 6 gives the results of experiments with fresh alloys treated previously at 400° in a stream of nitrogen (Experiments 1 and 3) carried out in parallel with experiments on the same alloys carbonized by the method described (Experiments 2 and 4). The fresh alloy tested in Experiment 5 was treated with the most readily decomposed reaction product, dichloroethylsilane, with the object of carbonizing the alloy. This was carried out by passing dichloroethylsilane vapor over alloy powder in the reactor at 400°, after which the alloy was used for the synthesis of chloroethylsilanes in the usual way (Experiment 6).

Reaction of Silicon-Copper Alloys with Alkali. A 20 g sample of fresh, spent, or carbonized alloy and 300 ml of 8% aqueous KOH were placed in a round-bottomed flask fitted with thermometer and sealed stirrer, and the mixture was heated at 50-55° for 20 minutes; the hydrogen liberated in the reaction was measured. The results of the experiments are given in Table 7.

SUMMARY

1. It was shown that in the interaction of silicon-copper alloys with ethyl chloride, their activities change greatly as the silicon reacts with formation of chloroethylsilanes.

2. It was found that for alloys of low copper content (5-9%) the curves for total activity and selectivity in the formation of dichlorodiethylsilane pass through two maxima (during the first hour of the synthesis and after 7-8 hours from the start of the synthesis), whereas for alloys of high copper content (about 25%) there is only one selectivity maximum (1-2 hours after the start of the synthesis) and only one total-activity maximum (3-4 hours after the start of the synthesis).

3. In accordance with the results of these investigations it was suggested that the interaction of ethyl chloride with silicon-copper alloys is made up of two simultaneous processes: a) reaction with the silicon of the intermetallic compound Cu_3Si with separation of active copper; b) reaction with free silicon in presence of the liberated copper, acting as a catalyst. On the basis of this hypothesis an explanation was given of the changes in activity of alloys of different copper contents.

4. It was shown that reduction in the selectivity and activity of the catalyst mass at the end of the synthesis is associated with reaction of most of the silicon, accumulation of copper, and the distribution of the copper over the surface of the particles of the catalyst mass. In the course of the reaction considerable amounts of carbon separate on the surface of the copper, and this also favors lowering of the total activity of the mass. However, the fact that the selectivity of the catalyst mass for the formation of dichlorodiethylsilane falls sharply at the end of the synthesis cannot be explained solely by the liberation of carbon.

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COMPOSITION OF THE RESIN ACIDS OF THE OLEORESINS OF PINUS PITHYUSA AND PINUS INSIGNIS

B. A. Arbuzov and A. G. Khismatullina

Work on the composition of the resin acids of the oleoresins of conifers, the isolation of individual resin acids, and the determination of their structures, which has now continued for more than a century, encounters great difficulties owing to the labile character of these acids and their tendency to form mixed crystals. As a result of these peculiar characteristics of resin acids, in addition to a few individual compounds, numerous "sapinic" and other acids have been described which have been found to be mixtures [1]. A great advance in the isolation and separation of mixtures of resin acids was brought about by the application of the amine salt method, first used by Balas in 1927 [2] and developed by the work of Palkin, Harris, and others [1, 3]. The quantitative analysis of resin acids has been greatly facilitated by the use of ultraviolet absorption spectra [3, 1]. The method of partition chromatography has recently been applied with success in the study of resin acids [4].

As a result of progress in methods of separating and isolating individual resin acids it was shown that relatively few individual resin acids are present in the oleoresins of various conifers. The presence of the following resin acids in the oleoresins of conifers has now been rigorously established: levopimaric, dextropimaric, neoabietic, abietic, isodextropimaric, dihydroabietic, and dehydroabietic acids [4]. As shown originally by Harris [5], abietic acid is a primary resin acid.

The development of quantitative methods of determining individual resin acids has made it possible to show that some resin acids which have been isolated from oleoresin in very small amount form a considerable part of the oleoresin (up to 40% of levopimaric acid, instead of the 1-2% isolated through the sodium salt).

In view of these considerations the study of the qualitative and quantitative compositions of resin acids of the oleoresins of various conifers presents considerable interest. In the present paper we give the results of a study of the composition of the resin acids of the oleoresins of two pines, Pinus pithyusa and Pinus insignis, collected by M. I. Ado in the Sochi region.

Composition of the Resin Acids of the Oleoresin of Pinus pithyusa

The oleoresin was obtained with the aid of a bleeding tube by A. E. Arbuzov's method under conditions which prevented evaporation of the volatile part; it was preserved in hermetically stoppered glass vessels. The oleoresin obtained in this way consisted of an almost colorless clear liquid together with resin acids that had crystallized out in the form of a snow-white clearly crystalline mass. The oleoresin contained 33.7% of turpentine, 35.9% of crystalline resin acids, and 30.0% of nonvolatile liquid. The composition of the turpentine was studied previously [6]. The resin acids, present in crystals and in solution in the turpentine, were investigated separately. The crystalline part of the oleoresin had $[\alpha]_D^{20}$ – 21.0° (in alcohol) and an acid value of 120, which corresponds to a content of resin acids of 90%.

In the study of the composition of the resin acids we used the method used by Harris in similar investigations [1]. Levopimaric acid was estimated by the change in the rotation of the resin acids when levopimaric acid was removed with the aid of acid-free maleic anhydride; its content was found to be 8%. It will be seen that the levopimaric acid content of the oleoresin of Pinus pithyusa is very small in comparison with that for other pines (30-40%). The further investigation of the composition of the crystalline resin acids was carried out spectroscopically.

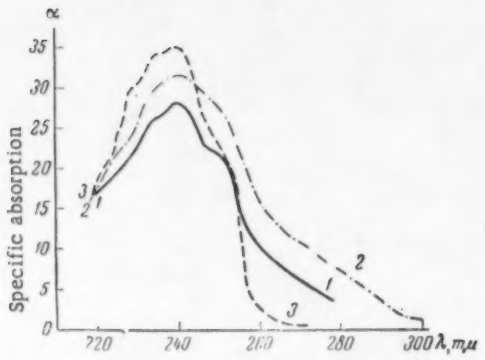

Fig. 1. Ultraviolet absorption spectrum of the resin acids of Pinus pithyusa: 1) original resin acids; 2) acids, freed from levopimaric acid; 3) resin acids isomerized with HCl.

Curve 1 (Fig. 1) gives the ultraviolet absorption spectrum of the original crystalline resin acids; Curve 2 gives the spectrum of the resin acids after removal of levopimaric acid by means of maleic anhydride. The presence of inflections in the absorption curve (Curve 1) in the region of 235 and 240 mμ indicates the presence of abietic acid, and the maximum at 250 mμ indicates the presence of neoabietic acid. Quantitative calculations, made by Harris's method, show that abietic acid amounts to 38% and neoabietic acid to 31% of the total quantity of acids. Hence, the amount of abietic and neoabietic acids in the crystalline part of the oleoresin of Pinus pithyusa is very large.

In order to confirm the amount of neoabietic acid, the resin acids were isomerized by means of hydrogen chloride. The absorption spectrum of the isomerized acids is represented by Curve 3 (Fig. 1). From the rise in the maximum at 240 mμ the amount of abietic acid, increased as a result of the isomerization of neoabietic and levopimaric acids into abietic acid, was found to be 80%, which confirms the previously found value (31%) for the amount of neoabietic acid. In order to determine the percent content of acids of the dextropimaric type, the original resin acids were isomerized in benzene solution with hydrogen chloride and treated with maleic anhydride. In this way levopimaric, abietic, and neoabietic acids were removed; after removal of the maleic anhydride adduct, the remaining acids were investigated spectrographically. The absorption spectrum of the residual acids is given in Fig. 2.

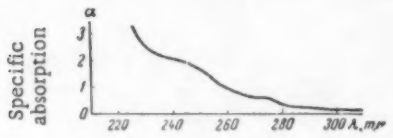

Fig. 2. Ultraviolet absorption spectrum of the residual resin acids of Pinus pithyusa.

The absorption spectrum of the residual acids indicates the absence of acids of the abietic type (absence of the maximum at 270 mμ characteristic for neoabietic acid). The residual resin acids amount to 16% of the total amount of acids.

The content of dextropimaric acid was determined by Sandermann's method [7] on the basis of the rotation of the plane of polarization, and it was found to be 7.7% on the total amount of acids in the oleoresin. The residual acids may include also the following resin acids: dehydroabietic acid, dihydroabietic acid, and isodextropimaric acid. The small maximum at 275 mμ on the absorption curve of the residual acids may indicate the presence of dehydroabietic acid [5]. Attempts to detect the presence of dihydroabietic acid by means of its insoluble lactone were not successful. Hence, the most probable second component of the residual acids is isodextropimaric acid.

In order to investigate the resin acids of the oleoresin of Pinus pithyusa which remained in solution, they were isolated in the form of the cyclohexylamine salt. The amount of resin acids in the liquid part of the oleoresin was 60%. After isolation of the free acids from the cyclohexylamine salt by means of boric acid, they were investigated as in the case of the crystalline resin acids. The free acids had $[\alpha]_D$ − 20.5° and an acid value of 132 (to sodium hydroxide).

The absorption spectra of the acids are given in the following curves in Fig. 3: Curve 1, original resin acids; Curve 2, after treatment with maleic anhydride; Curve 3, after isomerization with hydrogen chloride; Curve 4, residual acids of the pimaric type. The compositions of the resin acids isolated from the crystalline and liquid parts of the oleoresin were determined and are shown in Table 1.

Hence, the compositions of the resin acids that crystallized from the oleoresin and of those that remained in solution are identical.

TABLE 1

Composition	Crystalline part of the oleoresin	Liquid part of the oleoresin
Levopimaric acid	8	8
Abietic acid	38	40
Neoabietic acid	31	33
Dextropimaric acid	8	12
Isodextropimaric acid and others	15	7

The identification of the individual resin acids of Pinus pithyusa was carried out mainly by optical methods. In confirmation of the results we separated the individual resin acids via their characteristic amine salts. With this object the resin acids that crystallized from the oleoresin were converted into their dibutylamine salts. After several recrystallizations from methyl acetate a salt was isolated having m.p. 159-160° and $[\alpha]_D$ − 68°, which corresponds to the reported values (m.p. 159-161° and $[\alpha]_D$ − 69° [8]) for dibutylamine abietate. From the salt we isolated abietic acid, m. p. 172-173° and $[\alpha]_D$ − 105°. Neoabietic acid was isolated with the aid of its 2-amino-2-methyl-1-propanol ("butanolamine") salt.

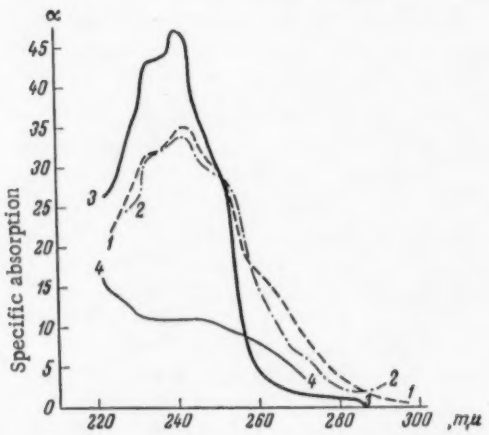

Fig. 3. Ultraviolet absorption spectrum of resin acids isolated from the liquid part of the oleoresin of Pinus pithyusa: 1) original acids; 2) acids freed from levopimaric acid; 3) acids isomerized with HCl; 4) residual acids.

For this purpose the crystalline resin acids freed from levopimaric acid by treatment in the cold with maleic anhydride were converted into their 2-amino-2-methyl-1-propanol salts. Recrystallization in accordance with the triangular scheme gave a fraction having $[\alpha]_D$ + 100°, which corresponds to the salt of neoabietic acid ($[\alpha]_D$ + 102° [3]). The absorption of the salt is shown in Fig. 4 (Curve 1).

Apart from this 2-amino-2-methyl-1-propanol salt, a salt having $[\alpha]_D$ ± 0°, corresponding to isodextropimaric acid, was isolated. The isodextropimaric acid isolated from the salt had m.p. 160-162° and $[\alpha]_D$ ± 0°; the literature [9] gives m.p. 162-164° and $[\alpha]_D$ ± 0°. The absorption spectrum of isodextropimaric acid is shown in Fig. 4 (Curve 2). In order to isolate dextropimaric acid, the residual acids of the nonabietic type were converted into 2-amino-2-methyl-1-propanol salts, and the salt of isodextropimaric acid was separated by crystallization. Dextropimaric acid, m.p. 220° and $[\alpha]_D$ + 76°, was isolated from the mother liquor; the literature [9] gives m.p. 217-219° and $[\alpha]_D$ + 79°. The absorption spectrum of dextropimaric acid is shown in Fig. 4 (Curve 2); it is identical to that of isodextropimaric acid.

Composition of the Resin Acids of the Oleoresin of Pinus insignis

The oleoresin of the pine Pinus insignis was obtained by Ado in the Sochi region by the bleeding-tube method. The composition of the volatile part was studied previously [10]. In view of the fact that for Pinus pithyusa no substantial difference was found between the resin acids that crystallized out and those that remained dissolved in the oleoresin, the resin acids of the oleoresin of Pinus insignis were isolated entirely via the difficultly soluble cyclohexylamine salt. The resin acids isolated from the salt had $[\alpha]_D$ − 90.6° (alcohol) and acid value 130, and they formed 58.5% of the oleoresin. Their absorption spectrum is shown in Fig. 5 (Curve 1). The amount of levopimaric acid was determined by the optical method after removal of levopimaric acid by means of maleic anhydride.

The absorption spectrum of the acids after treatment with maleic anhydride is shown in Fig. 5 (Curve 2). The amount of levopimaric acid was 35%. Abietic and neoabietic acids were determined from the change in rotation and absorption spectrum of resin acids isomerized with hydrogen chloride (Fig. 6). The amount of abietic acid was 6.5% and the amount of neoabietic acid was 14%. Dextropimaric acid was determined from the rotation of the plane of polarization of residual acids of the dextropimaric type (absorption spectrum, see Fig. 7) and amounted to 28% of the total resin acids. Isodextropimaric acid was not determined.

When we compare the composition of the resin acids of the oleoresins studied with that of resin acids from the oleoresins of other conifers, it can be seen (Table 2) that the resin acids of the oleoresin of Pinus pithyusa are distinguished by the low content of levopimaric acid and the high contents of abietic and neoabietic acids. The composition of the resin acids from the oleoresin of Pinus insignis is close to the compositions of the acids from the oleoresins of other conifers.

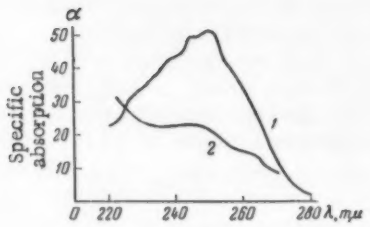

Fig. 4. Ultraviolet absorption spectra. 1) 2-amino-2-methyl-1-propanol salt of neoabietic acid isolated from the resin acids of Pinus pithyusa; 2) dextropimaric and isodextropimaric acids isolated from the oleoresin of Pinus pithyusa.

EXPERIMENTAL

Investigation of the Crystalline Resin Acids of the Oleoresin of Pinus pithyusa

The resin acids that crystallized from the oleoresin were filtered off under suction; they had $[\alpha]_D^{20}$ − 21° (alcohol) and acid value 120 (to sodium hydroxide).

In the determination of levopimaric acid the resin acids (50 g) were dissolved in ether and treated at room temperature with triple-distilled maleic anhydride. The ether solution was stirred for two hours, allowed to stand for several hours, and slowly added to 3% aqueous sodium hydroxide taken in the amount necessary for the neutralization of the acids; the solution was made up to 3 liters with distilled water, and the resin acids were regenerated with boric acid. Boric acid was added until the pH reached 6.2 (bromothymol blue). The ether extract was washed with water and dried with sodium sulfate; ether was distilled off. A difficultly crystallizable resin having $[\alpha]_D$ + 4° (alcohol) and acid value 130 was obtained. The estimation of levopimaric acid was carried out by the formula X = (C − B) (A − B), in which A, the rotation of pure levopimaric acid, is − 276°, B is the rotation of the resin acids after treatment with maleic anhydride, and C is the rotation of the original resin acids. The content of levopimaric acid was found to be 8%. The contents of abietic and neoabietic acids were determined spectrophotometrically by Harris's method [5]. The absorption spectra were determined in alcoholic solution with an SF-4 spectrophotometer.

For the determination of the content of acids of the dextropimaric type the resin acids (200 g) were dissolved in benzene; maleic anhydride was added to the solution, which was then saturated with dry hydrogen chloride. The benzene solution was heated in a water bath for 50 hours. Benzene was steam-distilled off, and the residue was washed with hot water to remove maleic anhydride and treated with a solution of sodium hydroxide; the solution was made up to 6 liters and stirred while dilute hydrochloric acid was added to pH 6.2 (bromothymol blue). The precipitated acids were extracted with ether. The ether solution was washed with water, dried with sodium sulfate, and evaporated. The residual acids had $[\alpha]_D$ + 14.3° (alcohol) and amounted to 33 g (16% on the total amount of acids).

The content of dextropimaric acid was determined by Sandermann's method [7]:

$$S = \frac{100\,[([\alpha]_{D\varepsilon}) + 104.2]}{183.5},$$

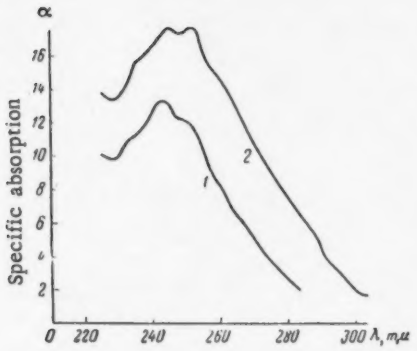

Fig. 5. Ultraviolet absorption spectrum of resin acids of the oleoresin of Pinus insignis: 1) original acids; 2) acids freed from levopimaric acid.

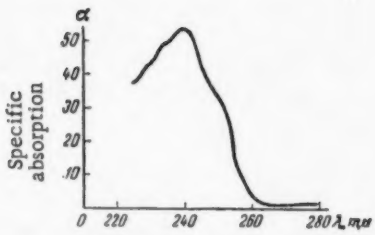

Fig. 6. Ultraviolet absorption spectrum of resin acids of Pinus insignis isomerized with HCl.

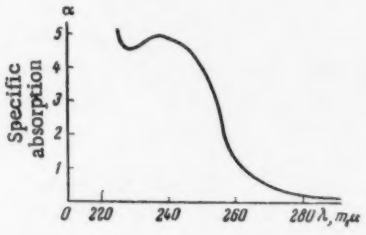

Fig. 7. Ultraviolet absorption spectrum of residual resin acids of Pinus insignis.

TABLE 2

Resin acids from the oleoresin of the pine	Levopimaric	Abietic	Neoabietic	Dextropimaric	Isodextropimaric
P. silvestris	35			18 [11]	
P. maritima	34.6			[12]	
P. palustris	30-35	15-20	15-20	8 [12]	8 [5]
P. caribbea	28.3				

in which 104.2 is the rotation of abietic acid and 183.5 = 104.2 + 79.3,(+ 79.3) being the rotation of dextropimaric acid; $[\alpha]_{D\epsilon}$ is the rotation of the isomerized acids and in this experiment had the value of $-90°$; S = 7.7%. The content of acids of the abietic type was confirmed by the isolation of the maleic anhydride adduct from the original acids that had been isomerized with hydrogen chloride and treated with maleic anhydride. From 200 g of acids we obtained 200 g (70%) of adduct, m.p. 220° and $[\alpha]_D - 24°$ (alcohol).

Investigation of the Resin Acids Isolated from the Liquid Part of the Oleoresin of Pinus pithyusa

The liquid part of the oleoresin (100 g) was dissolved in acetone, and an acetone solution of cyclohexylamine was added. The yield of cyclohexylamine salt was 80 g, which corresponds to 60% of resin acids in the liquid part of the oleoresin. The resin acids isolated from the salt by treating its ethereal solution with boric acid solution had $[\alpha]_D$ – 20.5° and acid value 132. The rotation of the acids after treatment with maleic anhydride changed from this value (– 20.5°) to + 2.45°. The rotation of the acids after isomerization with hydrogen chloride rose from – 20.5° to – 70.5°. The residual acids after the isomerization with hydrogen chloride amounted to 20% of the acids taken and had $[\alpha]_D$ + 13.5°.

Identification of the Acids Via Their Amine Salts

The crystalline part of the oleoresin (32 g, containing 28 g of resin acids) was dissolved in acetone and treated with an acetone solution of dibutylamine. After long standing 12 g of the dibutylamine salt, $[\alpha]_D$ – 35° (alcohol) and m.p. 141-143°, separated. Recrystallization from a large volume of methyl acetate gave 3.5 g of salt having $[\alpha]_D$ – 68° and m.p. 159-160°. Dibutylamine abietate has m.p. 159-161° and $[\alpha]_D$ – 69°. The abietic acid isolated with the aid of dilute hydrochloric acid and recrystallized from acetic acid had m.p. 172-173° and $[\alpha]_D$ – 102° (alcohol).

Identification of Neoabietic and Isodextropimaric Acids

With vigorous stirring, 40 g of resin acids freed from levopimaric acid by treatment with maleic anhydride in the cold was treated in acetone solution with an acetone solution of 2-amino-2-methyl-1-propanol. The product was 31 g of salts of m.p. 178-180° and $[\alpha]_D$ + 7.2° (alcohol). The 2-amino-2-methyl-1-propanol salts were recrystallized on the triangular scheme from a large amount of methyl acetate. In one experiment we obtained the following fractions: K_1(I), m.p. 183-185° and $[\alpha]_D$ + 11° (21 g); K_1 (II), $[\alpha]_D$ + 13° (17 g); K_1(III), $[\alpha]_D$ + 17° (11 g); K_2 (II), $[\alpha]_D$ + 32° (2.5 g); K_1 (IV), $[\alpha]_D$ + 15° (9.5 g); K_1 (V), $[\alpha]_D$ + 5° (7.5 g); K_1 (VI), $[\alpha]_D$ + 3° (6 g); K_1 (VII), $[\alpha]_D$ 0° (2 g); K_2 (III), $[\alpha]_D$ + 91° (11 g).

Recrystallization of K_2(III) from methyl acetate gave a fraction of the salt having $[\alpha]_D$ + 100°. The 2-amino-2-methyl-1-propanol salt of neoabietic acid has $[\alpha]_D$ + 102° [3]. Fraction K_1(VII), $[\alpha]_D$ ± 0°, corresponds to the 2-amino-2-methyl-1-propanol salt of isodextropimaric acid. The isodextropimaric acid regenerated from the salt with hydrochloric acid had m.p. 160-162° and $[\alpha]_D$ ± 0°, which is in accord with the literature [9].

For the isolation of dextropimaric acid, 20 g of the residual acids of the dextropimaric type was treated with an acetone solution of 2-amino-2-methyl-1-propanol; 19 g of 2-amino-2-methyl-1-propanol salts was isolated. After a series of recrystallizations from methyl acetate we obtained a salt fraction having $[\alpha]_D$ ± 0°, corresponding to the salt of isodextropimaric acid. The acetone solution of the remaining salts was evaporated to dryness; the residue was dissolved in ether, and the acids were separated out with 10% hydrochloric acid. The acids were dissolved in acetone, and the solution was cooled to – 20°. The precipitated acids were recrystallized from glacial acetic acid until the product had a constant rotation of + 76° and m.p. 220°.

Composition of the Resin Acids of the Oleoresin of Pinus insignis

The investigation was carried out in the same way as in the case of the oleoresin of Pinus pithyusa. The resin acids were isolated through the cyclohexylamine salt. The salt had $[\alpha]_D$ – 90.6°. After treatment with maleic anhydride it had $[\alpha]_D$ + 10°. From this it can be shown that the levopimaric content is 35%. After isomerization with hydrogen chloride: $[\alpha]_D$ – 58°. The residual acids had $[\alpha]_D$ + 38°.

Preparation of 2-Amino-2-methyl-1-propanol

1. Preparation of 2-Methyl-2-nitro-1-propanol. A few pieces of $KHCO_3$ and K_2CO_3 were added to a mixture of 175 g of 2-nitropropane (b.p. 115-117°) and 245 g of formalin; the mixture was shaken. Heat was evolved. The product was extracted several times with ether; the ether extract was dried with calcium chloride. Removal of ether gave 200 g of 2-methyl-2-nitro-1-propanol (90% yield), a yellow mass which was difficult to crystallize.

2. Preparation of 2-Amino-2-methyl-1-propanol. A mixture of 620 ml of water, 240 g of $FeSO_4 \cdot 7H_2O$, 20 g of H_2SO_4, and 440 g of iron powder was heated to 100°. Over a period of four hours 200 g of 2-methyl-2-nitro-1-propanol was added as a solution in 300 ml of water; heating was continued for one hour further. A kerosene fraction (1500 ml, b.p. 160-192°) was added, and kerosene was distilled off with return of the upper kerosene layer to the flask; 600 ml of kerosene was then distilled off, and the layers were separated. The aqueous layer was acidified, and water was evaporated off. The precipitate formed was treated with alkali and the amine layer was vacuum-distilled. The yield of amine was 100 g (67%); b.p. 72° (14 mm) and 88-90° (30 mm).

SUMMARY

1. The composition of the resin acids of the oleoresin of Pinus pithyusa was studied. The compositions of the resin acids that crystallized out and the resin acids that remained in solution were identical. The resin acids included: levopimaric acid 8%, abietic acid 35%, neoabietic acid 31%, dextropimaric acid 8%, isodextropimaric and other acids 15%.

2. The composition of the resin acids of the oleoresin of Pinus insignis was studied. The resin acids included: levopimaric acid 35%, abietic acid 6.5%, neoabietic acid 14%, and dextropimaric acid 24%.

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TRANSFORMATIONS OF n-UNDECANE IN PRESENCE OF VARIOUS GROUP VIII METALS AND HYDROGEN UNDER PRESSURE IN A FLOW SYSTEM

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In previous communications [1, 2] we reported results on the catalytic transformations of n-heptane and n-decane in presence of various Group VIII metals and hydrogen under pressure at high temperatures. Study of the catalysis products from these hydrocarbons showed that the following were the main reactions occurring: a) aromatization, b) skeletal isomerization, c) hydrogenolysis of the original hydrocarbons and their transformation products into hydrocarbons of lower molecular weight, and d) formation of cyclopentanes and cyclohexanes. We showed that the extent of the transformation of the hydrocarbons is to a great extent determined by the chemical nature of the metals used.

In the investigation of the 97-100° fraction separated as a result of precision fractionation of the catalyzate obtained in presence of $Ru-SiO_2$, we found not only unchanged n-heptane, but also about 5% of methylcyclohexane. This new observation of the direct formation of methylcyclohexane in the catalytic dehydrocyclization of n-heptane shows that the rate of the dehydrogenation of the intermediately formed methylcyclohexane into toluene over $Ru-SiO_2$ is lower than that of the cyclization of heptane. Spectroscopic investigation of the 65-100° fraction of the paraffin-naphthene part of the n-decane catalyzate showed that it consisted of a mixture of cyclopentanes (mainly methylcyclopentane) and isoparaffins. Judging from the aniline point (52,5°), this fraction contained about 55% of cycloalkanes. With the aid of Raman spectra we detected methylcyclohexane in admixture with C_8 isoparaffins in the 100-130° fraction; catalytic dehydrogenation of this over platinized charcoal at 300° gave a catalyzate in which, after sulfonation, decomposition of the sulfonic acid, and investigation of the ultraviolet absorption spectra, toluene was identified.

The formation of cyclopentanes and cyclohexanes under the given conditions is of special interest and shows that this process occurs not only under ordinary pressure over platinized charcoal of high platinum content (20%), as shown by Kazanskii, Liberman, and co-workers [3, 4], but also under a pressure of hydrogen over a platinum-alumina catalyst containing only 1% of platinum.

Continuing this line of investigation, in the present work we studied the behavior of n-undecane over Pt, Pd, and Ni catalysts. Hardly any work has been reported on the transformations of alkanes of high molecular weight. This is clearly explained by the fact that investigations of this sort meet various difficulties associated with the absence of chemical and physical methods of analyzing the hydrocarbon mixtures resulting from these transformations. However, progress in spectroscopy has made it possible to make an approach to the solution of this problem. A method that we have described previously [2] enables us to determine the degree of branching of higher alkanes by investigation of their infrared spectra. In the investigation of our catalyzates we used a combination of methods (precision fractionation, chromatographic adsorption, and Raman analysis), which enabled us to form a fairly clear picture of the transformation products of n-undecane.

EXPERIMENTAL

Synthesis of n-Undecane. The hydrocarbon was synthesized in two ways. 1) By the Grignard method from heptylmagnesium bromide and butyraldehyde, which gave undecyl alcohol; this was dehydrated to undecene over alumina in a flow system at 320°, and the undecene was hydrogenated at 220-225° over platinized charcoal (1% Pt) in a stream of electrolytic hydrogen. 2) From undecenoic acid, which was hydrogenated to the corresponding alcohol in an autoclave over a copper-chromium catalyst prepared by Adkins and Connor's method [5]; the

alcohol was converted into the hydrocarbon as in the first method. In both cases the hydrocarbon was vacuum-distilled through a column of 33 theoretical plates and then had the following properties: b.p. 128.2° (100 mm); 195.5-196° (760 mm); n_D^{20} 1.4172; d_4^{20} 0.7406; f.p. – 25.6°. For this hydrocarbon the literature [6] gives the following constants: b.p. 127.95° (100 mm) and 195.84° (760 mm); n_D^{20} 1.4172; d_4^{20} 0.7402 and f.p. – 25.65°.

Catalysts. As catalysts we used 0.5% of palladium and 0.5% of platinum on alumina and also 8% nickel on the same carrier. The alumina used for the preparation of the catalysts was calcined at 500° for 2.5-3 hours and then impregnated with hydrofluoric acid at such a strength that the dry alumina contained 0.5% of HF. The catalysts were reduced for 10-12 hours at 320-340° in a stream of electrolytic hydrogen.

Experimental Conditions. The experiments were carried out in an apparatus of the flow type [1] in presence of hydrogen at 20 atm; molar ratio H_2: undecane = 5; space velocity of feed of hydrocarbon = 1.1-1.2 hour^{-1}. The temperature varied from 350° to 450°. For each experiment 80-110 g of hydrocarbon was taken.

Investigation of the Catalyzates. The properties of the liquid catalyzates were characterized by determinations of density, refractive index, and content of aromatic hydrocarbons (by the sulfuric acid method). Before adsorption of aromatic hydrocarbons from the catalyzates, hydrocarbons boiling up to 40° were distilled off through a column of 33 theoretical plates. Aromatic hydrocarbons were then separated by chromatographic adsorption on silica gel; after separation they were fractionated and identified. Before separation of n-paraffins from iso-paraffins in the paraffin-naphthene part of the catalyzate with the aid of urea, hydrocarbons boiling up to 100° were distilled off. The remainder of the catalyzate was treated with urea, and the hydrocarbons obtained were fractionated. In order to establish their molecular composition the fractions were submitted to Raman spectrum analysis. The results are given in Tables 1-4.

As will be seen from Table 1, with rise in the temperature of the experiment, in all cases the extent of the conversion of undecane increases, though the different catalysts give quantitatively different results. The highest conversion is found over a palladium catalyst at 410°. There is a simultaneous increase in the content of saturated hydrocarbons in the gas. The extent of gas formation is particularly great over a nickel catalyst at 385°; hence, no experiments at higher temperatures were carried out with this catalyst. Increase in the amount of gaseous products was accompanied by increase in the amount of hydrocarbons boiling below 40° in the liquid catalyzate. Thus, in the case of a palladium catalyst the catalyzate obtained at 385° yielded 1.6% of 2-methylbutane and 1.2% of pentane, whereas the catalyzate obtained under the same conditions over a nickel catalyst yielded 1.6% of 2-methylbutane and 2.6% of pentane. Catalyzates obtained at 385° and 410° over platinized alumina contained neither 2-methylbutane nor pentane. The catalyzate obtained at 410° over Pd—Al_2O_3 contained 15% of 2-methylbutane and 12% of pentane.

TABLE 1

Properties of Undecane Catalyzates Obtained over Various Catalysts

Catalyst	Temperature of experiment (°C)	Properties of catalyzate			Conversion of undecane (%)	Composition of gas	
		n_D^{20}	d_4^{20}	Content of aromatic hydrocarbons (% vol.)		H_2 (%)	C_nH_{2n+2} (%)
0.5% Pd—Al_2O_3	350	1.4167	0.7398	—	10.9	99.0	1.0
	385	1.4145	0.7285	0.5	42.7	98.2	1.8
	410	1.4200	0.6994	12.0	67.2	82.2	18.8
0.5% Pt—Al_2O_3	350	1.4167	0.7405	—	3.7	99.0	1.0
	385	1.4160	0.7404	—	7.2	99.0	1.0
	410	1.4160	0.7371	2.0	10.2	96.0	4.0
	450	1.4162	0.7335	4.0	22.3	89.4	10.6
8% Ni—Al_2O_3	350	1.4160	0.7392	—	5.4	97.0	3.0
	385	1.4160	0.7359	3.0	20.0	70.0	30.0

TABLE 2

Properties of Aromatic Hydrocarbons Separated from Undecane Catalyzates

Catalyst	Amount of substance	Boiling range (°C)	Properties		Results of Raman analysis
			n_D^{20}	d_4^{20}	
$Pd—Al_2O_3$	18.6	102—108	1.4948	0.8618	Mainly toluene
		108—125	1.4963	0.8628	Mainly toluene
		125—150	1.4995	0.8661	Toluene (3-5%), p-xylene (5%), and m- and o-xylenes in equal amounts
		150—168	1.5020	0.8708	Pseudocumene and a small amount of m-ethyltoluene
$Pt—Al_2O_3$	9.7	108—125	1.4886	0.8608	Mainly toluene
		125—145	1.4838	0.8620	Toluene (traces), p-xylene (8-10%), and m- and o-xylenes in equal amounts
$Ni—Al_2O_3$	4.5	85—108	1.4910	—	Not investigated
		109—125	1.4940	0.8630	Mainly toluene
		125—145	1.4938	0.8614	Mainly xylenes with a predominance of o-xylene

The fractional compositions and properties of the aromatic hydrocarbons isolated from the catalyzates are given in Table 2. The same table gives the results of their Raman spectrum analysis. The results in Table 2 show that in the passage of undecane over the catalysts investigated various aromatic compounds are obtained which have fewer carbon atoms than the original hydrocarbon.

TABLE 3

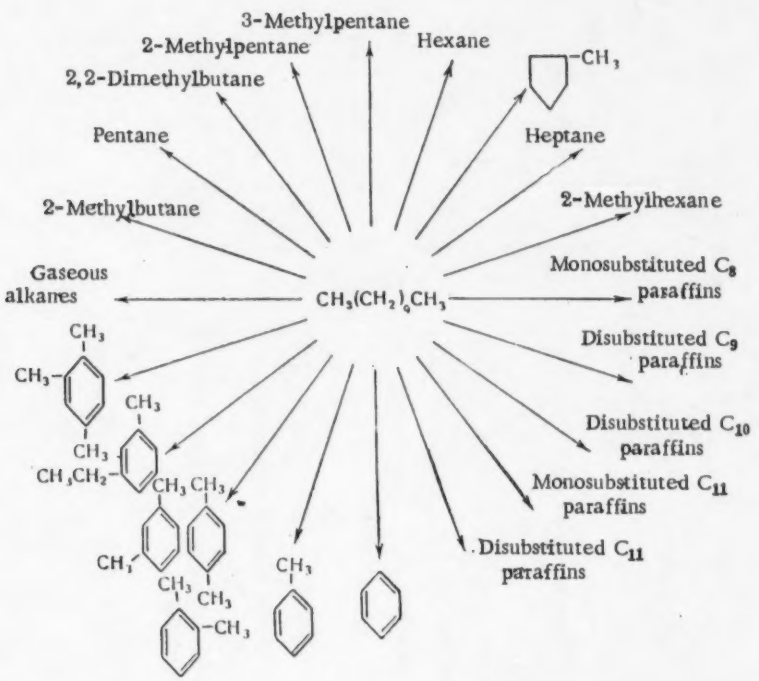
Normal Paraffins Separated by the Urea Treatment of Catalyzates Obtained over Various Catalysts at Various Temperatures

Substance	Catalyst								
	0.5% $Pd—Al_2O_3$			0.5% $Pt—Al_2O_3$				8% $Ni—Al_2O_3$	
	Temperature of experiment (°C)								
	350	385	410	350	385	410	450	350	385
Hydrocarbons distilling below n-undecane (g)	—	4.9	4.2	—	—	—	5.1	3.0	3.3
Ditto (% by weight on the catalyzate)	—	4.4	2.6	—	—	—	6.2	3.2	4.4
n-Undecane (g)	90.0	48.5	24.0	78.6	88.0	90.0	50.4	76.5	50.9
Ditto (% by weight on the catalyzate)	83.1	43.5	14.6	84.3	85.1	81.6	59.5	83.9	66.1

From the catalyzates, after removal of hydrocarbons boiling up to 40° and aromatic hydrocarbons, hydrocarbons boiling up to 100° were distilled off ; the residue was treated with urea in order to separate n-paraffins from isoparaffins. The hydrocarbons obtained by this treatment were subjected to precision fractionation and Raman analysis (Tables 3 and 4). In most cases, individual fractions obtained from catalyzates prepared over different catalysts but having identical properties (n_D^{20}, d_4^{20}, and boiling range) were combined and then subjected to Raman analysis.

From the catalyzate obtained over Pd–Al_2O_3 at 385° we isolated 7.0 g of a fraction that boiled up to 100° (6.6% calculated on the amount of catalyzate). The resulting mixture of hydrocarbons was separated into narrower fractions, which were then subjected to Raman spectrum analysis. The following hydrocarbons were identified: 2,2-dimethylbutane, 2-methylpentane, 3-methylpentane, methylcyclopentane, and heptane. From the catalyzate obtained over the same catalyst at 410° we isolated 23.4 g (14.6% calculated on the amount of catalyzate) of an analogous fraction. By fractionation and Raman spectrum analysis it was shown that it contained the following hydrocarbons: 2,2-dimethylbutane, 2-methylpentane, 3-methylpentane, methylcyclopentane, hexane, 2-methylhexane, and heptane. From the catalyzates obtained over Pt–Al_2O_3 at 385°, 410°, and 450°, we again isolated fractions boiling up to 100°, the amounts being 1.6 g (1.5% on the catalyzate), 2.7 g (2.4% on the catalyzate), and 4.2 g (5% on the catalyzate) respectively. In view of the very small amounts of these they were not analyzed in detail. From the catalyzate obtained over Ni–Al_2O_3 at 385° we isolated only 1.2 g (1.5% on the catalyzate) of such a head fraction.

Analysis of the experimental material obtained in the study of the transformations of undecane in presence of finely dispersed Pd, Pt, and Ni supported by alumina shows that this hydrocarbon, depending on the experimental conditions, undergoes various transformations. The reactions occurring under the given conditions may be represented by the following scheme:



The main transformations of undecane are isomerization, hydrocracking, and partial dehydrocyclization with formation of aromatic hydrocarbons of various molecular weights. The relative importance of the individual reactions depends on the temperature of the experiment and the chemical nature of the metal catalyst. Thus, whereas at 385° (other conditions being equal) over Pd–Al_2O_3 the conversion of the original hydrocarbon is 42.7%, over Pt–Al_2O_3 and Ni–Al_2O_3 the conversions are only 7.2% and 20.0% respectively. Again, in the case of Ni–Al_2O_3 the exit gas contained 30% of saturated hydrocarbons, whereas for Pt–Al_2O_3 and Pd–Al_2O_3 the figures were only 1.8% and 1.0% respectively. Hence, 8% Ni–Al_2O_3 brings about more profound hydrogenolysis of the original hydrocarbon than Pd–Al_2O_3 and Pt – Al_2O_3. As regards the considerable difference in the isomerizing properties of Pd–Al_2O_3 and Pt – Al_2O_3, these appear to depend not only on the chemical nature of the metal, but also on

TABLE 4

Fractional Compositions, Properties, and Results of Raman Spectrum Analysis for Isoparaffins Isolated from the Catalyzates after Treatment with Urea

Boiling range	Properties of combined fraction		Hydrocarbons found	Catalyst								
				0.5% Pd–Al_2O_3			0.5% Pt–Al_2O_3				8% Ni–Al_2O_3	
				Temperature of experiment (°C)								
	n_D^{20}	d_4^{20}		350	385	410	350	385	410	450	350	385
125—135	1.4060	0.7222	C_8 monosubstituted	—	1.0*	0.6	—	—	—	0.35	—	1.8
135—150	1.4152	0.7429	C_9 disubstituted	—	1.7	0.6	—	—	—	0.3	—	1.6
150—165	1.4170	0.7469	C_{10} disubstituted	0.5	1.6	0.5	—	—	—	0.5	—	1.8
165—175	1.4187	0.7481	Mainly C_{10} disubstituted	0.9	2.4	1.6	—	—	0.5	0.6	—	1.9
175—185	1.4190	0.7460	C_{11} disubstituted	1.6	6.3	5.2	—	1.2	1.4	1.8	1.3	2.1
185—188	1.4185	0.7440	C_{11} monosubstituted with predominant substitution in position 2	2.6	9.2	6.6	1.2	1.3	1.6	3.7	1.9	2.5
188—190	1.4183	0.7425	Mixture of C_{11} monosubstituted and n-undecane	4.7	10.9	8.6	1.4	1.9	1.9	5.9	1.7	3.5

* The figures are contents of isoparaffins in the catalyzate (% by weight).

the difference in "acidity" between the catalysts. The reduced catalysts were tested for pH (with an R-5 potentiometer), and values of 6.2 for Pd– Al_2O_3 and 8.3 for Pt –Al_2O_3 were found. The specific surfaces of these two catalysts were almost the same: 154 sq·m/g for Pd – Al_2O_3 and 160 sq·m/g for Pt–Al_2O_3.

As regards the aromatic hydrocarbons of various molecular weights present in the undecane catalyzates, these could be formed both as a result of direct dehydrocyclization of the original hydrocarbon with subsequent dealkylation and alkylation of the aromatic hydrocarbons formed, and also as a result of the dehydrocyclization of the hydrogenolysis products of undecane containing not less than six carbon atoms in their chains.

SUMMARY

1. An investigation was made into the catalytic properties of palladium, platinum, and nickel, finely dispersed at low concentration on an alumina carrier, in the transformations of n-undecane at 350-450° in presence of hydrogen at 20 atm in a flow system.

2. It was shown that the degree of conversion of the original hydrocarbon is largely determined by the nature of the catalyst.

3. It was shown that, under the given conditions, the transformations of undecane proceed mainly by isomerization, hydrocracking, and partial dehydrocyclization.

4. The ways in which aromatic hydrocarbons may be formed from undecane were discussed.

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**In Russian.

LIQUID-PHASE TRANSFORMATIONS OF m-XYLENE IN PRESENCE OF METAL HALIDES

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Study of the conditions for the catalytic transformation of m-xylene with the object of obtaining the p-isomer is now of great practical importance because of the use of p-xylene as the starting material for the synthesis of terephthalic acid. As is well known, terephthalic acid is used in the manufacture of high-quality synthetic fibers [1] which have found extensive application. The problem of increasing the supply of p-xylene arises because of the very low content of this isomer in the mixture of C_8 aromatic hydrocarbons. m-Xylene, on the other hand, forms the greater part of xylene fractions of petroleum, of products of the thermal treatment of coal and petroleum, and of products of the catalytic cracking and reforming of petroleum distillates; in chemical respects it is at present of less value than the other two isomers.

The separation of the mixture of xylenes is effected by precision fractionation [2] (separation of o-xylene) and low-temperature crystallization [1, 3] (separation of p-xylene from m-xylene). This is now the preferred method and is applied on the manufacturing scale. Thermodynamic calculations [4] show that the isomerization of m- and o-xylenes into p-xylene is possible. Thus, as a result of the isomerization of m-xylene at 127° the following equilibrium mixture of C_8 aromatic hydrocarbons is formed: 55.8 moles % of m-xylene, 18.6 moles % of o-xylene, 23.8 moles % of p-xylene, and 1.8 moles % of ethylbenzene.

Various papers have appeared also on the transformations of m-xylene in presence of aluminum chloride [5-12]. The main object of these investigations was the study of the conditions for the simplification of the xylene molecule with formation of benzene and toluene [8, 10, 12] and the study of the character of methyl transfer, both within a given molecule and from one xylene molecule to another [5-7, 12]. The conditions for the rearrangement of methyl groups in xylenes in presence of aluminum chloride were studied by Norris and Vaala [11]. Like previous investigators [5-7], they also established the presence of p-xylene in the products of the transformation of m-xylene in contact with aluminum chloride. In all these investigations the conditions used were close to those required for the Friedel-Crafts reaction. The reaction products included toluene and considerable amounts of trimethylbenzenes, in addition to the three isomeric xylenes.

It is unfortunately impossible to reach any definite conclusions about the optimum conditions for the isomerization of m-xylene into p-xylene in presence of aluminum chloride from an examination of data available in the literature. This is probably to be explained by the fact that the investigations cited did not have the object of obtaining p-xylene as reaction product. There are no data in the literature on the transformations of m-xylene in presence of other metal chlorides.

In the present paper we report experimental material obtained in the study of the transformations of m-xylene in presence of aluminum chloride and bromide and also of Sb, Sn, Ti, and Zn chlorides and their equimolemixtures with aluminum chloride. We showed that aluminum chloride and bromide isomerize m-xylene into p-xylene to equal extents. We found the most suitable conditions for carrying out this reaction, namely: temperature 100°, amount of aluminum chloride 5% by weight, duration of contact 4 hours. The p-xylene content of the hydrocarbon mixture obtained under optimum conditions was close to the equilibrium composition [4]. Comparison between experimental and calculated data is given in Table 1.

TABLE 1

Composition of Hydrocarbon Mixture obtained in the Isomerization of m-Xylene in presence of $AlCl_3$ (5%) Duration of contact 4 hours

Hydrocarbon	Composition of catalyzate (moles %) obtained in experiment at 100°	Equilibrium concentration at 127° (moles %) [4]
p-Xylene	20.3	23.8
m-Xylene	52.5	55.8
o-Xylene	9.3	18.6
Ethylbenzene	—	1.8
Toluene	7.0	—
C_9 aromatic hydrocarbons	5.0	—
Intermediate fractions	4.3	—
Losses in fractionation	1.6	—

As regards Sb, Sn, Ti, and Zn chlorides, under the same conditions they bring about the isomerization of m-xylene into p-xylene only to a slight extent (about 5%). However, stannic chloride and antimony chloride in admixture with an equimolecular amount of aluminum chloride appreciably suppress the drastic effects of the latter, which result in the formation of by-products, in particular toluene and trimethylbenzenes.

EXPERIMENTAL

For investigation we took pure m-xylene obtained from the Khar'kov Coke Chemicals Factory; it had the following constants: b.p. 137° (740 mm); n_D^{20} 1.4973 and d_4^{20} 0.8642. In the investigation of the Raman spectrum of the original hydrocarbon, the other isomers were not detected. As catalysts we used chemically pure anhydrous aluminum, titanium, tin, and zinc chlorides, and also chemically pure anhydrous aluminum bromide.

TABLE 2

Characteristics of m-Xylene Catalyzates obtained by Treatment with $AlCl_3$ and $AlBr_3$

Experiment	Catalyst	Weight of catalyst (%)	Temperature of experiment (°C)	Duration of experiment (hours)	Yield of liquid catalyzate (% by weight)	Properties of catalyzate		Content of individual hydrocarbons in catalyzate (% by wt.)*				
						n_D^{20}	d_4^{20}	Toluene	p-Xylene	o-Xylene	m-Xylene	C_9 aromatic hydrocarbons
1	$AlCl_3$	5	18	4	98.8	1.4972	0.8642	—	Traces	—	100	—
2	Ditto	5	100	2	98.6	1.4972	0.8644	—	8.2	10.3	74.5	—
3	" "	5	100	4	98.8	1.5001	0.8670	6.3	20.0	9.5	51.4	5.5
4	" "	5	100	4	99.7	1.5001	0.8668	2.0	12.1	2.7	74.0	2.8
5	" "	5 (fresh)	100	4	100.0	1.4989	0.8652	2.0	4.0	2.6	90.1	—
6	" "	5	120	4	89.0	1.4994	0.8676	13.7	18.4	8.0	37.6	15.0
7	" "	5	120	4	99.4	1.4988	0.8670	2.8	13.0	3.2	73.5	3.0
8	" "	5	120	4	99.8	1.4978	0.8652	3.0	5.0	—	90.0	—
9	" "	10	120	4	91.3	1.4982	0.8673	22.0	15.0	7.3	30.0	18.5
10	" "	5	137 (b.p.)	4	92.6	1.5002	0.8736	15.0	15.3	7.4	35.4	15.8
11	" "	5	137 (b.p.)	24	92.2	1.5012	0.8730	22.6	12.0	11.3	28.2	18.1
12	$AlBr_3$	5	18	4	99.4	1.4973	0.8646	—	Traces	—	100	—
13	Ditto	5	100	4	93.0	1.4985	0.8674	4.5	18.0	7.7	61.0	0.2
14	" "	10	100	4	90.6	1.4988	0.8676	7.2	20.0	9.1	41.7	8.7
15	" "	5	120	4	95.0	1.4990	0.8680	4.5	15.0	10.3	60.2	2.9

* No account is taken in the table of aromatic hydrocarbons contained in the head fraction (up to 108°) and intermediate fractions.

All experiments on the catalytic treatment of m-xylene with these metal chlorides and aluminum bromide were carried out in a three-necked flask fitted with mechanical stirrer, thermometer immersed in the reaction mixture, and condenser. For each experiment 50 g of m-xylene was taken. In experiments with aluminum chloride and bromide the reaction temperature, the time of contact, and the amount of catalyst were varied. When the operation was complete, the hydrocarbon layer was separated from the complex, washed (first with water, then with 10% sodium carbonate solution, and again with water until the reaction was neutral), and dried with calcined calcium chloride.

After preliminary treatment the catalyzates were subjected to precision fractionation through a column of 35 theoretical plates. The following fractions were collected: up to 108°, 108-112° (toluene), 112-135° (toluene-xylene), 135-140° (p- and m-xylene), 140-145° (o-xylene), 145-154° (cumene with o-xylene impurity), 154-160° (propylbenzene with cumene impurity), 160-165° (mesitylene with pseudocumene impurity), and 165-170° (pseudocumene with mesitylene impurity). From the catalyzates obtained in Experiments 6, 9, 10, and 11 (Table 2) fractions boiling in the ranges 170-187° and 187-220° were separated. These fractions amounted to 3.7% and 3.4% respectively. The total yield of intermediate fractions from the catalyzate did not exceed 5.5%. The refractive indices and densities of the fractions were determined. The hydrocarbon composition of the main fractions was determined with the aid of Raman spectra.* The characteristics of the m-xylene catalyzates and the contents of the individual isomers are given in Tables 2 and 3.

TABLE 3

Transformations of m-Xylene in presence of $ZnCl_2$, $TiCl_4$, $SnCl_4$, and $SbCl_3$ and their Equimolecular Mixtures with $AlCl_3$ (100°, 4 hours)

Experiment	Catalyst	Yield of liquid catalyzate (% by weight)	n_D^{20}	d_4^{20}	Content of individual hydrocarbons in catalyzate (% by wt.)*				
					Toluene	o-Xylene	p-Xylene	m-Xylene	Trimethylbenzenes
1	$ZnCl_2$	99.5	1.4973	0.8642	—	—	5.0	95.0	—
2	$ZnCl_2 \cdot AlCl_3$	94.0	1.4992	0.8676	12.0	14.0	15.3	40.4	12.2
3	$TiCl_4$	100.0	1.4968	0.8638	—	—	5.0	95.0	—
4	$TiCl_4 \cdot AlCl_3$	94.0	1.4990	0.8680	5.0	17.2	17.0	48.3	5.8
5	$SnCl_4$	100.0	1.4975	0.8642	—	—	5.0	95.0	—
6	$SnCl_4 \cdot AlCl_3$	95.0	1.4975	0.8646	—	5.0	17.0	78.0	—
7	$SbCl_3$	98.4	1.4970	0.8646	—	—	5.0	95.0	—
8	$SbCl_3 \cdot AlCl_3$	95.2	1.4975	0.8652	2.4	5.7	16.0	70.3	—

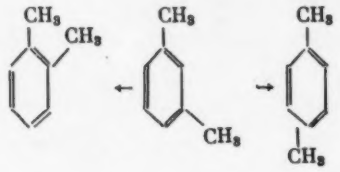
The experimental results given in Table 2 enable us to conclude that the most favorable conditions for the isomerization of m-xylene into p-xylene are: 100°, 4 hours contact, 5% of catalyst on the original hydrocarbon. Rise in the temperature at which the isomerization of m-xylene is carried out (Experiments 6 and 10, Table 2) to 120° and 137° (boiling point of the reaction mixture) results in increase in the extent of the conversion of m-xylene, but the p-xylene content of the catalyzates obtained under these conditions is lowered from 20% (Experiment 3, Table 2) to 18.4% and 15.3% respectively. At the same time the yield of toluene rises to 22% and the content of C_9 aromatic hydrocarbons in the catalyzate (mesitylene and pseudocumene) is 15-18.1%. With increase in the amount of aluminum chloride to 10% (Experiment 9, Table 2) the yield of p-xylene falls to 15% and the contents of toluene and trimethylbenzenes in the catalyzate rise to 22% and 18.5% respectively. Similar results are obtained when the temperature is raised to 137° (boiling point of m-xylene) and the duration of the experiment is increased to 24 hours (Experiments 10 and 11, Table 2). Fractions of b.p. 170-187° and 187-220° obtained from the catalyzates formed in Experiments 6-11 were combined and investigated by the Raman spectrum method. The analysis showed that these fractions contained 1,2,4-trimethylbenzene, 1,2- and 1,4-diethylbenzenes, 1,2,4,5-tetramethylbenzene, and traces of naphthalene.

All isomerization experiments with Sn, Sb, Zn, and Ti chlorides and their equimolecular mixtures with aluminum chloride were carried out under similar conditions: 10% (on the original hydrocarbon) of catalyst,

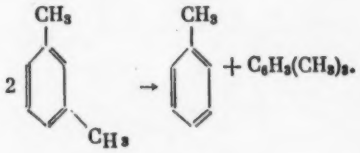
* Raman spectra were determined by Iu. P. Egorov, to whom the authors express their thanks.

4 hours, 100°. The characteristics and compositions of the catalyzates are given in Table 3. Table 3 shows that $SnCl_4$ and $SbCl_3$ are satisfactory additions to aluminum chloride: trimethylbenzenes are completely absent in catalyzates obtained in presence of these double chlorides, and the yield of p-xylene attains 17-16% by weight. In catalyzates obtained in presence of $AlCl_3 \cdot ZnCl_2$ and $AlCl_3 \cdot TiCl_4$, there is an appreciably greater content of o-xylene (which rises as high as 17%); moreover, trimethylbenzenes are formed (in amounts of 12.2% and 5.8% respectively).

Hence, the detailed investigation of the catalyzates obtained by the transformation of m-xylene shows that under our conditions m-xylene undergoes partial isomerization into the p- and o-isomers:



In addition to the isomerization of m-xylene there occur also demethylation of m-xylene into toluene and its methylation with formation of trimethylbenzenes:



SUMMARY

1. A study was made of the transformations of m-xylene in presence of aluminum halides and also in presence of Sn, Ti, Sb, and Zn chlorides and their equimolecular mixtures with aluminum chloride.

2. It was shown that in presence of $AlCl_3$ or $AlBr_3$ m-xylene undergoes isomerization with formation of 18-20% by weight of p-xylene. This yield is 75.6-85.2% of the equilibrium value.

3. It was found that addition of $SbCl_3$ or $SnCl_4$ to aluminum chloride results in suppression of the drastic effects of aluminum chloride alone with almost complete elimination of side reactions of demethylation and methylation.

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STEREOCHEMISTRY OF CYCLIC COMPOUNDS

COMMUNICATION 19. INFRARED SPECTRA OF POLYCYCLIC LACTONES

V. F. Kucherov, I. V. Berezin, and I. N. Nazarov

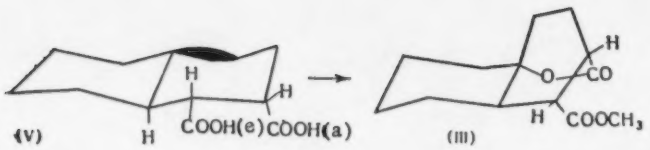
On the basis of many examples it has now been strictly established that the C=O bond of the alkoxycarbonyl group in esters of carboxylic acids has a characteristic absorption band at 1738-1740 cm^{-1} [1]. The same carbonyl absorption band is characteristic also for monocyclic δ-lactones [2], but the five-membered γ-lactone ring has a carbonyl frequency of about 1770 cm^{-1}. This difference in the infrared spectra of γ- and δ-lactones, corresponding to a difference of about 30 cm^{-1}, has been cited in various cases in support of the structures of certain terpenoid lactones [3] and was applied recently in the study of the lactonization of isomeric acids of the bicyclo (2.2.1) hept-2-ene series [4].

As shown in a previous communication [5], the method of infrared spectroscopy can be applied successfully for the confirmation of the structure of lactones formed in the lactonization of isomeric 1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acids. With the object of making a systematic study of the dependence of the infrared spectra on the structure and configuration of various polycyclic lactones, we determined the spectra of carbonyl frequencies for previously prepared lactones and lactone acids of the decahydronaphthalene and norcamphane (bicyclo [2.2.1] heptane) series.

As the first objects of investigation we selected the isomeric lactone esters (I), (II), and (III) and the lactone (IV); for three of these [(I), (II), and (IV)] the structure and configuration of the γ-lactone rings have been proved rigorously by means of stereospecific chemical transformations [5]. However, the isomeric lactone ester (III), in accordance with the configuration of the original anti-cis-1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acid [6], cannot have a similar structure and must have a δ-lactone ring. This we succeeded in confirming by the infrared spectra given in Table 1.

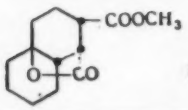
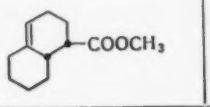
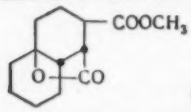
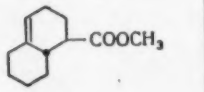
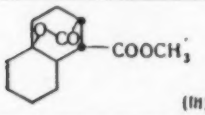
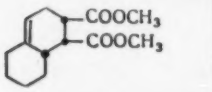
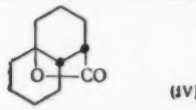
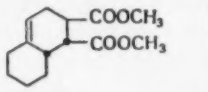
In accordance with their structures, the lactone esters (I) and (II) have two carbonyl absorption bands, one of which (about 1740 cm^{-1}) corresponds to the methoxycarbonyl group, and the other (about 1780 cm^{-1}) to the γ-lactone ring. The same carbonyl band (1779 cm^{-1}), which is displaced from that of simple γ-lactones by about 10^{-1} toward the short waves, is possessed also by the γ-lactone (IV). Such lowering of the γ-lactone carbonyl frequency is an intrinsic property of polycyclic γ-lactones and is probably to be explained by the effect of the cyclic decahydronaphthalene system. This view is confirmed by the fact that the absorption bands of the methoxycarbonyl groups of the same lactone esters, as also of various esters of isomeric 1,2,3,5,6,7,8,8a-octahydro-1-naphthalenecarboxylic acids, are completely in accord with data in the literature.

The infrared spectrum of the lactone ester (III), unlike those of (I), (II), and (IV), has a lactone absorption band at 1765 cm^{-1} (in addition to the normal methoxycarbonyl band), which is displaced by 15 cm^{-1} toward the long waves, as compared with γ-lactone esters. This shift, which is similar to that for simple lactones (though somewhat less), shows that the lactone ester (III) has a δ-lactone structure but is formed with considerable strain. This conclusion is in accord with molecular models, from which it can be seen that the lactonization of the original anti-cis-1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acid (V) can proceed only through the axial carboxyl at C-2 as a result of severe deformation of the chair form of the B ring:



Infrared spectra were determined also for isomeric lactone esters of the decahydromethylnaphthalene series (VI), (VII), and (VIII), prepared previously by the lactonization of isomeric adducts of 1-vinyl-1-cyclohexene with citraconic anhydride and with mesaconic ester [7] (Table 2).

TABLE 1

Formula of substance	Lactone carbonyl, ν (cm^{-1})	Ester carbonyl ν (cm^{-1})	Formula of substance	Ester carbonyl ν (cm^{-1})
 (I)	1782	1741		1735
 (II)	1780	1738		1739
 (III)	1765	1741		1740
 (IV)	1779	—		1740

It was found that all these lactone esters have carbonyl absorption frequencies of about 1740 cm^{-1} and 1780 cm^{-1}, corresponding to the presence of a free methoxycarbonyl group and a γ-lactone ring. These facts show that the previously described lactone acids do indeed possess γ-lactone structures and their formation proceeds as a result of the lactonization of the corresponding acids at the carboxy group at C-1. This structure for the lactones was proved also chemically, for it was found that the γ-lactone ester (VII), owing to the presence of an axial methoxycarbonyl at C-2, is capable of being isomerized by sodium methoxide into the more stable γ-lactone ester (VI), in which the methoxycarbonyl group is disposed equatorially.

The fact that the lactone esters (VI), (VII), and (VIII) have γ-lactone structures gives us reason to suppose that the diene condensation of 1-vinyl-1-cyclohexene with citraconic anhydride proceeds in accord with the general scheme of the diene synthesis with formation of a syn-cis adduct, and does not proceed contrary to this scheme, as was assumed previously [8]:

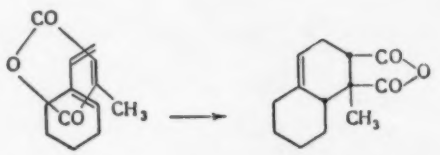
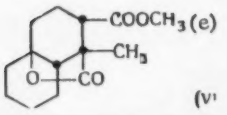
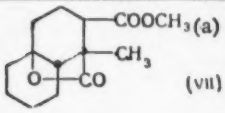
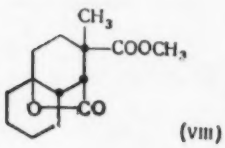
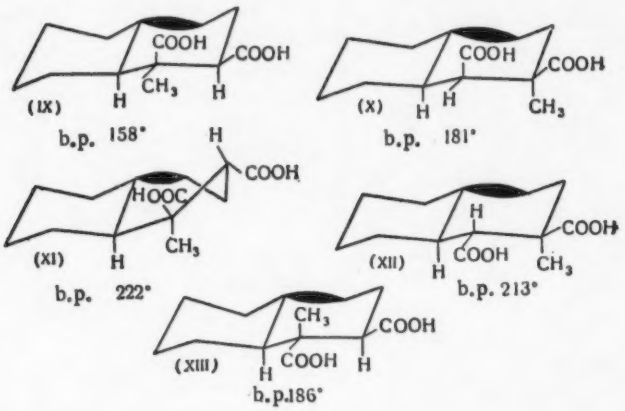


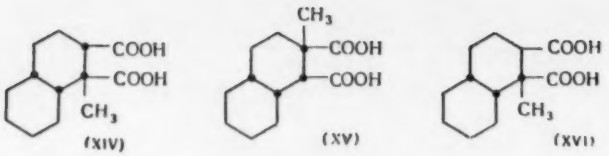
TABLE 2

Formula of substance	Lactone carbonyl, ν (cm^{-1})	Ester carbonyl, ν (cm^{-1})
 (V)	1781	1734
 (VII)	1779	1736
 (VIII)	1779	1741

In accordance with general steric laws, which we have proved previously for 1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acids [9], all five of the previously described isomeric 1,2,3,5,6,7,8,8a-octahydromethyl-1,2-naphthalenedicarboxylic acids (IX)–(XIII) must have configurations corresponding to the following spatial models:



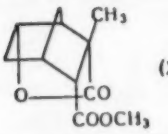
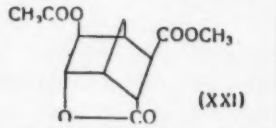
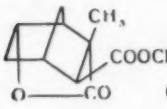
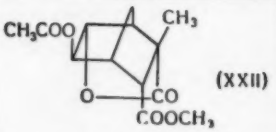
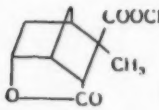
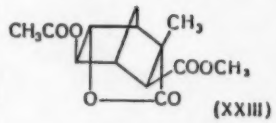
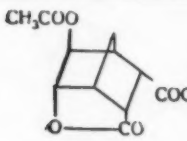
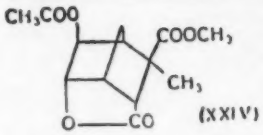
Such spatial structures for the isomeric acids correspond most completely with all the observed regularities of lactonization and the spatial orientation of hydrogenation. Only for such configurations can the isomers (IX), (X), and (XI) be capable of lactonization with formation of γ-lactones and can the lactone ester (VII), obtained from the acid (XI), be an epimer of the γ-lactone ester (VI) with respect to the carboxyl at C-2. Only with such configurations would the acids (XII) and (XIII) be capable of lactonization and would their hydrogenation proceed nonselectively (as it does in fact proceed). Owing to the screening effect of the carboxy groups of the isomeric acids (IX), (X), and (XI), their hydrogenation is sterically selective, and the saturated acids formed [(XIV), (XV), and (XVI)] must belong to the cis-decahydronaphthalene series and have the following configurations:



b.p. 178° b.p. 190° b.p. 229°

It is not difficult to see that, if the condensation of 1-vinyl-1-cyclohexene with citraconic anhydride were to proceed in the direction opposite to that required by the rule of "accumulation of unsaturation", as erroneously assumed previously [9], then all the rules of lactonization and hydrogenation would be reversed, which is in conflict with the experimental facts cited above.

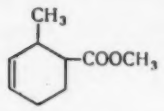
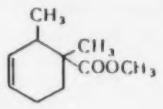
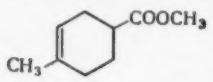
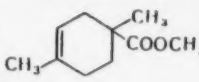
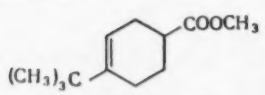
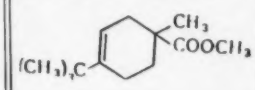
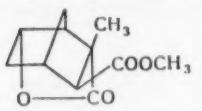
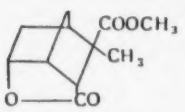
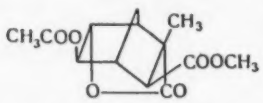
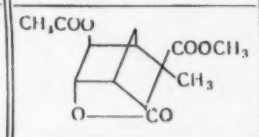
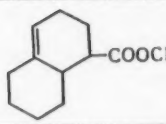
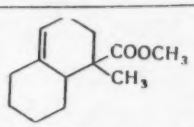
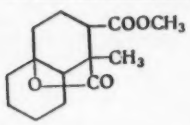
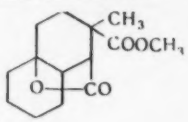
TABLE 3

Formula of substance	Lactone carbonyl, ν (cm^{-1})	Ester carbonyl, ν (cm^{-1})	Formula of substance	Lactone carbonyl, ν (cm^{-1})	Ester carbonyl, ν (cm^{-1})
 (XVII)	1777	1737	 (XXI)	1795	1738
 (XVIII)	1781	1736	 (XXII)	1786	1744
 (XIX)	1782	1732	 (XXIII)	1788	1739
 (XX)	1789	1746	 (XXIV)	1789	1732

The carbonyl frequencies of various γ-lactone esters of the norcamphane series, the structures of which were proved previously [10], differ somewhat from those of the above-described γ-lactone esters of the decahydronaphthalene series. As the data cited show, in the case of the γ-lactone esters (XVII)–(XIX), the carbonyl frequencies of the γ-lactone and methoxycarbonyl groupings are identical with those of the γ-lactone esters described above, and therefore they do not depend essentially on the presence of a fixed boat form of the cyclohexane ring. However, introduction of the acetoxy group in the lactone esters (XX)–(XXIV) leads to an appreciable shift of the lactone absorption band toward the short waves. It is characteristic that this shift occurs despite the trans disposition of the lactone and acetoxy groups. An analogous shift occurs also for the methoxycarbonyl band in the case of its cis arrangement with respect to the lactone ring [(XX) and (XXII)] (Table 3).

In the course of our study of infrared spectra we noted certain laws governing the dependence of the carbonyl frequencies of secondary and tertiary methoxycarbonyl groups on the character of the cyclic systems. It was found that in monocyclic systems and γ-lactones of the norcamphane series the carbonyl frequency of a secondary methoxycarbonyl group is displaced by 5-7 cm^{-1} toward the short waves with respect to the carbonyl frequency of the tertiary methoxycarbonyl group (Table 4).

TABLE 4

Formula of substance	Ester carbonyl, ν (cm^{-1})	Formula of substance	Ester carbonyl, ν (cm^{-1})
	1741		1737
	1744		1739
	1743		1739
	1737		1732
	1739		1732
	1735		1742
	1734		1741

A somewhat different relationship is found in the case of esters of the decahydronaphthalene series. In these compounds it is the carbonyl band of the tertiary methoxycarbonyl group that is displaced toward the short waves. However, these observations are not sufficiently complete and require confirmation.

EXPERIMENTAL

The spectra were determined with an IKS-11 apparatus having a rock salt prism; it was modified for automatic recording and fitted with a device for the automatic opening of the slit. The monochromator and illuminant

were subjected to a stream of dry air in order to prevent the appearance of water bands in the spectra as far as possible. The cell thickness was 0.24 mm. Carbon tetrachloride was used as solvent; the concentration of the solution was about 0.06 M. The limits of accuracy of the determination of the position of the carbonyl bands was ± 2 cm^{-1}.

SUMMARY

1. The infrared spectra of various cyclic lactones and lactone acids of the decahydronaphthalene and norcamphane series were studied in the region 1700-1800 cm^{-1}, and the structures of these compounds were confirmed. Some structural and steric regularities were noted for the carbonyl compounds of compounds of these classes.

2. By analysis of the infrared spectra of lactones of 1- and 2-methyldecahydro-1,2-naphthalenedicarboxylic acids the configurations of these compounds were established and corrections were introduced into previous conclusions concerning the stereochemistry of the diene condensation of 1-vinyl-1-cyclohexene with citraconic anhydride.

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*Original Russian pagination. See C. B. Translation.
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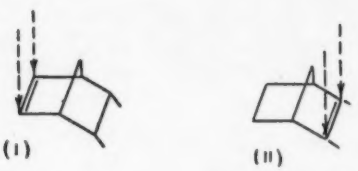
STEREOCHEMISTRY OF CYCLIC COMPOUNDS

COMMUNICATION 20. STEREOCHEMISTRY OF THE OXIDATION OF ISOMERIC BICYCLO[2.2.1]HEPT-5-ENE-2,3-DICARBOXYLIC ACIDS AND THEIR DERIVATIVES WITH PEROXYACETIC ACID

I. N. Nazarov, V. F. Kucherov, and V. G. Bukharov

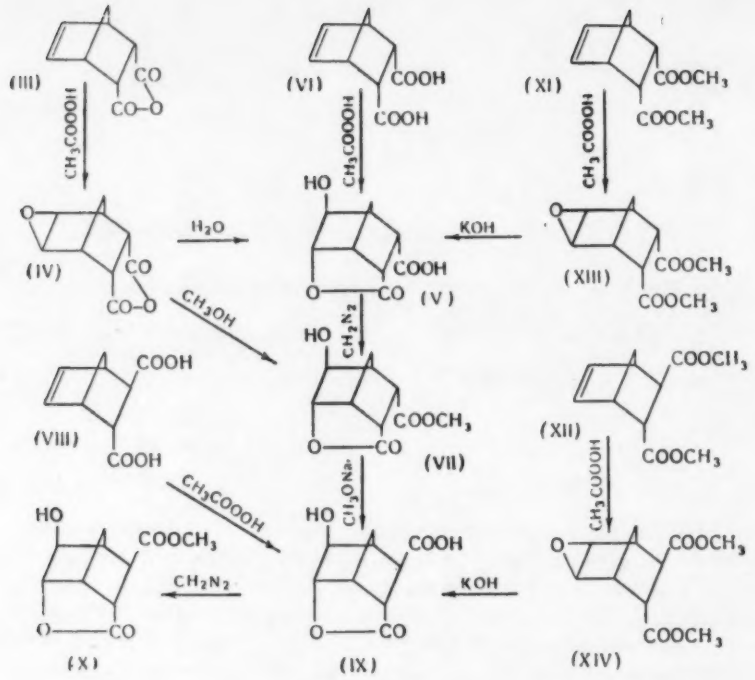
It has been shown in several cases that addition reactions at the double bond in bicyclo[2.2.1]hept-2-ene systems are stereospecific and proceed only from the same side as the methylene bridge (exo addition). In systems of type (I) it is in this direction that addition proceeds with cyclopentadiene [1], phenyl azide [2], bromine [3], and some other substances [4], and in the products the added groups take up the exo position. Addition reactions proceeding from the exo side occur also in systems of type (II) [5], and in this case even catalytic hydrogenation [6] gives products of endo structure almost quantitatively. Such stereospecificity of the addition reactions results from the presence in the bicyclo[2.2.1]hept-2-ene molecule of a fixed boat form of the cyclohexene ring, which has a greater screening effect than the methylene bridge so that exo-addition reactions occur:



(I) (II)

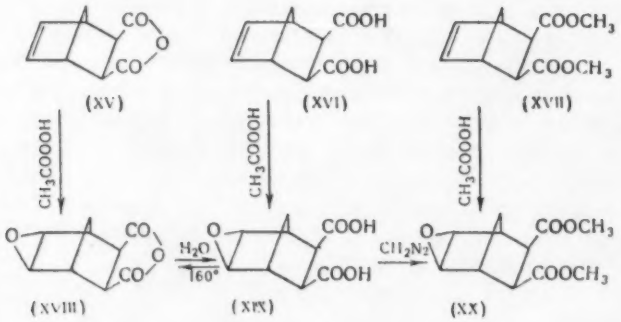
We considered that it would be of interest to study the stereochemistry of the oxidation of isomeric bicyclo [2.2.1]hept-5-ene-2,3-dicarboxylic acids and their derivatives with peroxyacetic acid, because in this case it is possible to prove the configuration of the epoxy ring with the aid of stereospecific lactonization and hydrogenation reactions. By the investigations that we have carried out we have succeeded in solving some questions of the stereochemistry of such compounds and the results obtained form the subject of the present paper.

In the oxidation of the endo anhydride (III) with excess of peroxyacetic acid in chloroform, only one crystalline exo epoxide (IV) was formed, and this was quantitatively lactonized when hydrolyzed with water with formation of the hydroxy γ-lactone acid (V). This last compound is obtained in good yield also in the direct oxidation of the endo acid (VI), and with diazomethane it gives the corresponding hydroxy γ-lactone ester (VII). Such ready lactonization of the exo epoxide (IV) is probably the result of intramolecular endo addition of the carboxyl group, for the hydroxy γ-lactone ester (VII) is formed quantitatively even when the epoxide (IV) is boiled with absolute methanol. The structure of the lactonization products was proved by the fact that the infrared spectrum of the hydroxy γ-lactone ester (VII) has a carbonyl absorption band at 5.6 μ, which is characteristic for a γ-lactone ring [7]. The exo position of the hydroxy group in the hydroxy lactone acid (V) follows from the fact that the compound was found to be incapable of forming a dilactone and gave only the corresponding acetic ester when boiled with acetyl chloride.

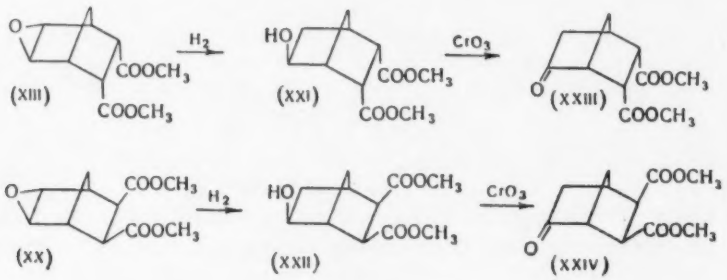


Oxidation of the trans acid (VIII) also proceeds with the formation of only one hydroxy γ-lactone acid (IX), which gives the corresponding hydroxy γ-lactone ester (X) with diazomethane. As would be expected, the hydroxy γ-lactone acid (IX) is an epimer of the hydroxy γ-lactone acid (V) at the free carboxy group; we confirmed this by isomerization of the hydroxy γ-lactone ester (VII) with sodium methoxide into the hydroxy γ-lactone acid (IX). This last fact shows that in such hydroxy lactone acids the exo position of carboxy and hydroxy groups is the more stable.

The oxidation of the endo and trans diesters (XI) and (XII), unlike that of the free acids, is not accompanied by lactonization, and quantitative yields were obtained of the corresponding epoxides (XIII) and (XIV), which are lactonized only after alkaline hydrolysis. Oxidation of compounds of the exo series also does not result in lactonization. The exo anhydride (XV), exo acid (XVI), and exo diester (XVII) give good yields of the corresponding stable epoxides (XVIII), (XIX), and (XX) when treated with peroxyacetic acid; and when these epoxides are boiled with water their epoxide rings do not open owing to the exo position of the carboxy groups. This fact shows that the epoxide ring is fairly stable and can open readily only when intramolecular lactonization is possible owing to the endo position of at least one of the carboxy groups.



In order to prove the configuration of the epoxide ring in all of the epoxides that we prepared, we used the hydrogenation reaction, which is known to proceed with preservation of the configuration at the carbon atom to which the oxygen of the epoxide ring remains attached. It was found that hydrogenation of the epoxy endo and exo diesters (XIII) and (XX) in presence of a nickel catalyst (140°, 120 atm) gives good yields of the pure hydroxy diesters (XXI) and (XXII), the presence in which of secondary hydroxy groups was proved by oxidation to the keto esters (XXIII) and (XXIV).



The hydroxy endo diester (XXI) after hydrolysis under acid conditions and the hydroxy exo diester (XXII) after hydrolysis under alkaline conditions were found to be incapable of lactonization, although it is known that free endo carboxy groups are formed in these treatments. It is not difficult to see that this can be true only in the case when the hydroxy group in the hydroxy diesters (XXI) and (XXII) has the exo configuration. These results show that the epoxide ring in all the epoxides that we have prepared has the exo position and that the oxidation of the isomeric bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acids with peroxyacetic acid is an exo-addition reaction.

EXPERIMENTAL

Oxidation of endo-cis-Bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic Anhydride (III)

A 100% excess (5 ml) of 70% peroxyacetic acid was added to a solution of 5 g of the endo anhydride (III) [8] in 70 ml of dry chloroform, and the mixture was heated for four hours at 45-50°. Solvent was distilled off under reduced pressure, the residue was treated with benzene, and the crystalline product was filtered off. Crystallization from dioxane gave 1.4 g of the epoxide (IV), m.p. 247-248°.

Found %: C 60.04; 60.08; H 4.36; 4.51
$C_9H_8O_4$. Calculated %: C 60.0; H 4.48

Hydroxy γ-Lactone Acid (V)

a) Peroxyacetic acid (2.4 ml of 70%) was added to a solution of 2 g of the endo acid (VI) in 10 ml of glacial acetic acid. After five days at room temperature the crystalline reaction product was filtered off, washed with ether, and recrystallized from acetone. The hydroxy γ-lactone acid (V), amounting to 1.4 g (65%), had a constant m.p. of 202-203°; found M 200.6 (titration); calculated M 198.2.

Found %: C 54.44; 54.67; H 5.10; 5.07
$C_9H_{10}O_5$. Calculated %: C 54.54; H 5.08

b) The above-described epoxide (IV) (0.5 g) was boiled with 2 ml of water until solution was complete. The crystalline product that separated on cooling was filtered off, and we then obtained 0.4 g of the hydroxy γ-lactone acid (V), m.p. 202-203°, undepressed by admixture of the previous sample.

Hydroxy γ-Lactone Ester (VII)

a) A solution of 0.5 g of the hydroxy γ-lactone acid (V) in 20 ml of benzene was treated with ethereal diazomethane. Solvents were distilled off under reduced pressure, and the crystalline residue was recrystallized from benzene. The yield of the hydroxy γ-lactone ester (VII), m. p. 91-92°, was 0.4 g.

Found %: C 56.52; 56.62; H 5.70; 5.66
$C_{10}H_{12}O_5$. Calculated %: C 56.60; H 5.70

When crystallized from water the hydroxy γ-lactone ester (VII) gave a crystal hydrate of m.p. 62-64°. Boiling of the hydroxy γ-lactone ester (VII) with acetyl chloride gave a good yield of the corresponding acetic ester, m.p. 76-77° after recrystallization from a 2:3 benzene-ether mixture.

Found %: C 56.58; 56.72; H 5.52; 5.55
$C_{12}H_{14}O_6$. Calculated %: C 56.68; H 5.55

b) A solution of the epoxy endo anhydride (IV) (0.5 g) in 60 ml of absolute ethanol was boiled for one hour. Methanol was distilled off under reduced pressure, and the residue was treated with ether. Crystallization from benzene gave 0.4 g of the hydroxy γ-lactone ester (VII), m.p. 91-92°, identical to the previous product.

Hydroxy γ-Lactone Acid (IX)

a) Peroxyacetic acid (2.4 ml of 70%) was added to a solution of 2 g of trans-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid (VIII) [9] in 10 ml of glacial acetic acid, and the mixture was left for two days at room temperature. The crystalline oxidation product was filtered off; recrystallization from an acetone-dioxane mixture gave 1.3 g of the hydroxy γ-lactone acid (IX), which melted constantly at 204-205°. The lactone acid (IX) shows depression when mixed with the above-described isomeric hydroxy γ-lactone acid (V); found M 202.0 (titration); calculated M 198.2.

Found %: C 54.9; 54.70; H 5.18; 5.05
$C_9H_{10}O_5$. Calculated %: C 54.54; H 5.08

Treatment of the hydroxy γ-lactone acid (IX) with ethereal diazomethane gave a quantitative yield of the hydroxy γ-lactone ester (X), which melted at 143-144° after crystallization from benzene.

Found %: C 56.51; 56.56; H 5.53; 5.67
$C_{10}H_{12}O_5$. Calculated %: C 56.60; H 5.70

Boiling of the hydroxy γ-lactone ester (X) with acetyl chloride gave the corresponding acetic ester, m.p. 96-97°, which is in accord with the literature [9].

b) The hydroxy γ-lactone ester (VII) (1.5 g) was added to a solution of 3.5 g of sodium in 90 ml of absolute methanol, and the mixture was boiled for 15 hours. The methanol was distilled off under reduced pressure, and the residue was dissolved in water, boiled for two hours, and filtered; the solution was acidified with hydrochloric acid and then evaporated to dryness under reduced pressure. Extraction with dioxane and crystallization from dioxane-acetone mixture gave 0.8 g of the hydroxy γ-lactone acid (IX), m.p. 204-205°, identical with the sample described above.

Oxidation of the endo Diester (XI)

Cooling was applied while 6.2 ml of 90% peroxyacetic acid was added to a solution of 8 g of the endo diester (XI) [10] in 40 ml of dry chloroform, and the mixture was left overnight at 0°. The chloroform solution was washed with water and with sodium bicarbonate solution, and was then dried with sodium sulfate. Removal of solvent under reduced pressure gave 7.5 g of the epoxide (XIII), m. p. 44-47°, raised to 46-57° by crystallization from ether.

Found %: C 58.46; 58.39; H 6.41; 6.42
$C_{11}H_{14}O_5$. Calculated %: C 58.40; H 6.23

Hydrolysis of the epoxide (XIII) with 10% sodium hydroxide solution gave a good yield of the above-described hydroxy γ-lactone acid (V), m.p. 202-203°.

Oxidation of the trans Diester (XII)

Cooling was applied while 9 ml of 90% peroxyacetic acid was added to a solution of 11 g of the trans diester (XII) [10] in 50 ml of dry chlorofom, and the mixture was left overnight at 0°. After being washed with water and sodium bicarbonate solution, the chloroform solution was dried over sodium sulfate; solvent was

distilled off. Vacuum distillation of the residue gave 11 g of the epoxide (XIV), b. p. 131-132° (3 mm); n_D^{20} 1.4820; d_4^{20} 1.2536; found MR 51.36; calculated MR 51.35.

Found %: C 58.21; 58.04; H 6.29; 6.25
$C_{11}H_{14}O_5$. Calculated %: C 58.40; H 6.23

Hydrolysis of the epoxide (XIV) with 10% sodium hydroxide solution readily gave the above-described hydroxy γ-lactone acid (IX), m.p. 204-205°, which was characterized in the form of its methyl ester, m.p. 143-144°.

Oxidation of the exo Anhydride (XV)

Cooling was applied while 4.8 ml of 90% peroxyacetic acid was added to a solution of 4 g of the exo anhydride (XV) [9] in 30 ml of dry chloroform, and the mixture was left overnight. Solvent was partially evaporated, and the crystalline product was filtered off and washed with a little cold chloroform. Crystallization from dioxane gave 2 g of the epoxide (XVIII), which melted constantly at 207-208°.

Found %: C 60.0; 59.60; H 4.48; 4.51
$C_9H_8O_4$. Calculated %: C 60.0; H 4.48

Oxidation of the exo Acid (XVI)

Peroxyacetic acid (1.5 ml of 90%) was added to a solution of 1.6 g of the exo acid (XVI) [11] in 8 ml of glacial acetic acid, and the mixture was left for two days at room temperature. Some of the acetic acid was distilled off under reduced pressure, and the crystalline product was filtered off and washed with ether. The epoxide (XIX), amounting to 1.45 g, had a decomposition temperature of 159-160°, which remained unchanged after crystallization from water. Found M 199.0 (titration); calculated M 198.2.

Found %: C 54.97; 54.85; H 5.26; 5.48
$C_9H_{10}O_5$. Calculated %: C 54.54; H 5.08

Hydrolysis of the Epoxide (XVIII)

The epoxy exo anhydride (XVIII) (0.8 g) was boiled with 1.5 ml of water until solution was complete; cooling gave 0.6 g of the epoxy exo acid (XIX), m.p. 159-160°, identical with the product described above. When this epoxide was heated at 170° for one hour it was converted quantitatively into the epoxy exo anhydride (XVIII), m.p. 207-208°.

Oxidation of the exo Diester (XVII)

Cooling was applied while 7.8 ml of 90% peroxyacetic acid was added to a solution of 9.5 g of the exo diester (XVII) [10] in 40 ml of dry chloroform, and the mixture was left overnight. The solution was washed with water and with sodium bicarbonate solution; it was dried with sodium sulfate, and chloroform was distilled off. The product (9 g) was the epoxide (XX), m.p. 85-87°; after crystallization from ether it melted at 87-88°, which is in accord with data in the literature [9]. The same epoxide was obtained quantitatively when the epoxy exo acid (XIX) was treated with ethereal diazomethane.

Hydrogenation of the Epoxy endo Diester (XIII)

Nickel catalyst (1 g) was added to a solution of 4.3 g of the epoxy endo diester (XIII) in 50 ml of dry cyclohexane, and the mixture was heated in a rotating autoclave for 2.5 hours at 140° in presence of hydrogen at 120 atm. The catalyst was filtered off, solvent was distilled off, and vacuum distillation of the residue gave 2.5 g of the hydroxy endo diester (XXI), b.p. 165-167° (4 mm), which gradually solidified; it melted at 66-68° after crystallization from a 3 : 1 mixture of ethyl ether and petroleum ether.

Found %: C 58.10; 58.13; H 7.10; 7.15
$C_{11}H_{16}O_5$. Calculated %: C 57.88; H 7.07

Treatment of the hydroxy endo diester (XXI) with acetyl chloride gave a good yield of the corresponding acetic ester in the form of a viscous liquid, b.p. 149-150° (2 mm); n_D^{20} 1.4770.

Found %: C 57.74; 57.67; H 6.77; 6.86
$C_{13}H_{18}O_6$. Calculated %: C 57.77; H 6.71

In the hydrolysis of the hydroxy endo diester (XXI) with 10% hydrochloric acid, no crystalline product corresponding to the normal lactonization reaction could be isolated.

Dimethyl endo-cis-5-Oxo-2,3-norcamphanedicarboxylate (XXIII)

A solution of 0.7 g of chromium trioxide in acetic acid was added to a stirred solution of 1.5 g of the hydroxy endo diester (XXI) in 20 ml of glacial acetic acid at 40-45°; stirring at this temperature was continued for five hours. The excess of chromium trioxide was removed by addition of methanol, the solution was evaporated to dryness under reduced pressure, and the residue was extracted with boiling benzene. The benzene solution was washed with water and benzene was distilled off; the product, amounting to 1 g, was the keto diester (XXIII) in the form of a thick oil, which did not crystallize when treated with various solvents; the semicarbazone, prepared in the usual way, melted at 214-215° after crystallization from methanol.

Found %: C 50.65; 50.81; H 6.08; 6.16; N 15.30; 15.11
$C_{12}H_{17}O_5N_3$. Calculated %: C 50.87; H 6.05; N 14.83

Hydrogenation of the Epoxy Diester (XX)

The epoxy exo diester (XX) (8.7 g) was hydrogenated as a solution in 50 ml of cyclohexane in presence of 2 g of nickel catalyst under a pressure of hydrogen of 120 atm (140°, 2.5 hours). Vacuum distillation of the hydrogenation product gave 7 g of the hydroxy exo diester (XXII) in the form of a viscous liquid, b.p. 158-159° (3 mm); n_D^{20} 1.4910.

Found %: C 57.72; 57.74; H 7.15; 7.15
$C_{11}H_{16}O_5$. Calculated %: C 57.88; H 7.07

Boiling of the hydroxy exo diester (XXII) with acetyl chloride followed by distillation gave a good yield of the corresponding acetic ester, b.p. 152-153° (3 mm); n_D^{20} 1.4755

Found %: C 57.77; 57.58; H 6.73; 6.70
$C_{13}H_{18}O_6$. Calculated %: C 57.87; H 6.71

Alkaline hydrolysis of the hydroxy exo diester (XXII) did not result in the isolation of any crystalline product having lactone character.

Dimethyl exo-cis-5-Oxo-2,3-norcamphanedicarboxylate (XXIV)

The hydroxy exo diester (XXII) (1.6 g), as a solution in acetic acid, was oxidized with excess of chromium trioxide at 40-45°; the mixture was evaporated to dryness under reduced pressure, and the residue was extracted with benzene. The benzene solution was washed with water; removal of solvent gave 1.1 g of the keto diester (XXIV), m.p. 82-84° (from ether).

Found %: C 58.17; 58.12; H 6.23; 6.10
$C_{11}H_{14}O_5$. Calculated %: C 58.40; H 6.23

The semicarbazone, prepared in the usual way, melted at 146-147° (from methanol).

Found %: N 15.13; 15.19
$C_{12}H_{17}O_5N_3$. Calculated %: N 14.83

SUMMARY

1. An investigation was made into the stereochemistry of the oxidation of isomeric bicyclo[2.2.1]hept-2-ene-2,3-dicarboxylic acids and their derivatives with peroxyacetic acid, and the reactions of the resulting epoxides were studied.

2. It was shown that, owing to the presence of free endo carboxy groups, the oxidation of the endo and trans dicarboxylic acids (VI) and (VIII) proceeds with formation of only the hydroxy γ-lactone acids (V) and (IX), the structures of which were proved by their mutual transformations.

3. Hydrogenation of the epoxides (XIII) and (XX) under pressure gave high yields of the corresponding hydroxy esters (XXI) and (XXII), which by oxidation with chromium trioxide were converted into the corresponding keto esters (XXIII) and (XXIV).

4. On the basis of hydrogenation and some other reactions it was proved that the oxidation of isomeric bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acids and their derivatives proceeds from the exo side and leads to epoxides in which the epoxide ring is in the exo position.

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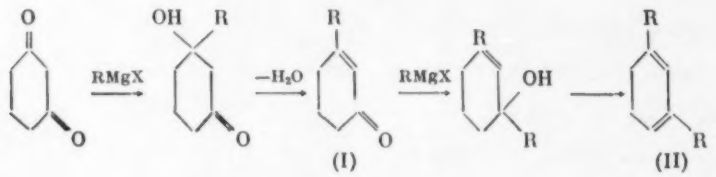
REACTION OF ORGANOMAGNESIUM COMPOUNDS WITH 2-BROMO-1,3-CYCLOHEXANEDIONE

I. N. Nazarov and S. I. Zav'ialov

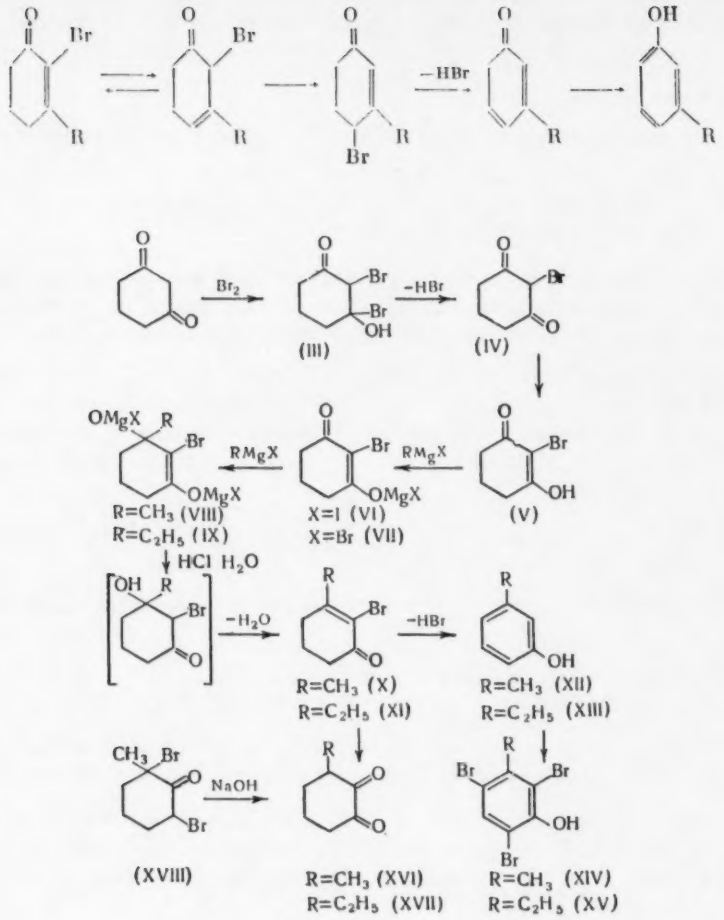
It is known [1] that bromination of 1,3-cyclohexanedione in chloroform solution gives the dibromo compound (III), and a short treatment of this at the boil with water eliminates hydrogen bromide and gives 2-bromo-1,3-cyclohexanedione (IV). We found that the bromination of 1,3-cyclohexanedione can be carried out also in aqueous solution, and this enabled us to obtain 2-bromo-1,3-cyclohexanedione in 60% yield with the isolation of the intermediate dibromo compound (III).

The bromine atom of 2-bromo-1,3-cyclohexanedione, unlike that of other α-bromo ketones, is not very mobile in nucleophilic reactions; thus it withstands treatment with caustic alkali or alkoxides for many hours at room temperature. Owing to the presence of the β-diketone grouping, 2-bromo-1,3-cyclohexanedione has marked acidic properties and displaces carbonic acid from its salts [1]. In connection with these peculiarities of 2-bromo-1,3-cyclohexanedione, it was of interest to study its reaction with organomagnesium compounds. Data in the literature [2, 3] indicate that 1,3-cyclohexanedione itself undergoes the Grignard reaction with formation of a mixture of the unsaturated ketone (I) and the diene (II) in accordance with the scheme:



It was found that, unlike 1,3-cyclohexanedione, 2-bromo-1,3-cyclohexanedione reacts with organomagnesium compounds in a strictly selective manner. By the action of methylmagnesium iodide or ethylmagnesium bromide, the magnesium enolate (VI) or (VII) is formed at first, and with excess of Grignard reagent this then gives the dimagnesium derivative (VIII) or (IX). This last compound is converted into the unsaturated bromo ketone (X) or (XI) by acidification with dilute hydrochloric acid. Hence, one of the keto groups of 2-bromo-1,3-cyclohexanedione is protected in the form of the magnesium enolate and therefore does not undergo the Grignard reaction. The undistilled bromo ketones (X) and (XI), the yields of which were 47% and 70% respectively, gave quantitative yields of characteristic bright-red 2,4-dinitrophenylhydrazones.

When vacuum-distilled (20-30 mm), the bromoketones (X) and (XI) lost hydrogen bromide and were converted in 45% and 55% yields into the m-substituted phenols (XII) and (XIII), which were characterized as the corresponding tribromo derivatives (XIV) and (XV). Partial elimination of hydrogen bromide was observed even during the distillation of the bromo ketones at a residual pressure of 2 mm from a bath at 130-140°, and we succeeded in obtaining an analytically pure product only in the case of 2-bromo-3-ethyl-2-cyclohexen-1-one (XI). This interesting reaction occurs probably as a result of displacement of the double bond into the β,γ-position with subsequent allyl migration of the halogen atom:



It is important to note that, despite the considerable structural similarity between the bromo ketones (X) and (XI) and the enol form of 2-bromo-1,3-cyclohexanedione (V), their bromine atoms differ greatly in chemical properties. The bromine atoms of the bromo ketones (X) and (XI) are exceptionally mobile: in a short treatment with dilute alkali in the cold they are replaced by hydroxy groups with formation of the cyclic α-diketones (XVI) and (XVII). 3-Methyl-1,2-cyclohexanedione (XVI) does not show melting point depression in admixture with an authentic sample obtained by a known method from the dibromo derivative of 2-methylcyclohexanone (XVIII)[4].

The transformations that we have investigated open up new possibilities for the synthesis of various m-substituted phenols and cyclic α-diketones from 1,3-cyclohexanedione.

EXPERIMENTAL

Bromination of 1,3- Cyclohexanedione. Bromine (16 g) was added dropwise to a stirred cooled (ice water) solution of 11.2 g of 1,3-cyclohexanedione in 250 ml of water. The resulting suspension of the dibromo compound (III) was heated at a gentle boil until the precipitate dissolved completely. The filtered solution was cooled. Washing of the reprecipitated material with ether gave 11.5 g (60%) of 2-bromo-1,3-cyclohexanedione (IV), m.p. 162-164° (from alcohol) [1].

Reaction of Methylmagnesium Iodide with 2-Bromo-1,3-cyclohexanedione. Dry, finely ground 2-bromo-1,3-cyclohexanedione (19.1 g, i.e., 0.1 mole) was added in portions to a stirred cooled (ice water) Grignard

reagent (0.25 mole) prepared from 6 g of magnesium and 36 g of methyl iodide in 400 ml of dry ether. The reaction mixture was allowed to stand for 24 hours at room temperature and was then decomposed with ice and dilute (1 : 1) hydrochloric acid. From the ether layer we isolated 9 g (47%) of 2-bromo-3-methyl-2-cyclohexen-1-one (X), which distilled with partial elimination of hydrogen bromide at 70-110° (2 mm).

Found %: Br 40.85; 41.04
C_7H_9OBr. Calculated %: Br 42.3

The 2,4-dinitrophenylhydrazone, after being washed with methanol, melted with decomposition at 164-165°.

Found %: Br 21.32; 44;* N 15.38; 15.46
$C_{13}H_{13}O_4BrN_4$. Calculated %: Br 21.7; N 15.2

When 2-bromo-1,3-cyclohexanedione reacted with the equivalent amount of methylmagnesium iodide under the above-indicated conditions, the magnesium enolate (VI) was formed, and on treatment of this with hydrochloric acid the 2-bromo-1,3-cyclohexanedione was recovered almost quantitatively.

Reaction of Ethylmagnesium Bromide with 2-Bromo-1,3-cyclohexanedione. The reaction was carried out as indicated above. Reaction between 19.1 g (0.1 mole) of 2-bromo-1,3-cyclohexanedione and ethylmagnesium bromide (0.25 mole) prepared from 6 g of magnesium and 30 g of ethyl bromide in 400 ml of ether gave 14.2 g (70%) of 2-bromo-3-ethyl-2-cyclohexen-1-one (XI), which distilled with partial elimination of hydrogen bromide at 116-120° (2 mm); n_D^{20} 1.5540.

Found %: Br 39.03; 38.91
$C_8H_{11}OBr$. Calculated %: Br 39.41

The 2,4-dinitrophenylhydrazone, after being washed with methanol, melted with decomposition at 154-155°.

Found %: Br 20.51; 20.64; N 15.12; 15.23
$C_{14}H_{15}O_4BrN_4$. Calculated %: Br 20.9; N 14.9

Reaction of 2-bromo-1,3-cyclohexanedione with the equivalent amount of ethylmagnesium bromide gave the magnesium enolate (VII), and hydrolysis of this resulted in regeneration of the 2-bromo-1,3-cyclohexanedione.

Conversion of 2-Bromo-3-methyl-2-cyclohexen-1-one into m-Cresol. Distillation of 10 g of 2-bromo-3-methyl-2-cyclohexen-1-one (X) at 27 mm gave 2.6 g (45%) of m-cresol, b. p. 101-103° (25 mm), m.p. 2-3°. By bromination of the m-cresol in an aqueous medium we obtained the tribromo derivative (XIV), which showed no depression of melting point when mixed with a known sample [5].

Conversion of 2-Bromo-3-ethyl-2-cyclohexen-1-one into m-Ethylphenol. Distillation of 15 g of 2-bromo-3-ethyl-2-cyclohexen-1-one (XI) at 27 mm gave 5.1 g (55%) of m-ethylphenol (XIII), b.p. 117-121° (27 mm); n_D^{20} 1.5350, and m.p. – 4° [6]. The tribromo derivative of m-ethylphenol (XV) melted at 77-78° (from aqueous alcohol).

Found %: Br 66.92; 67.05
$C_8H_7OBr_3$. Calculated %: Br 66.7

Conversion of 2-Bromo-3-methyl-2-cyclohexen-1-one into 3-Methyl-1,2-cyclohexanedione. A mixture of 11 g of 2-bromo-3-methyl-2-cyclohexen-1-one (X) and 6 g of sodium hydroxide in 100 ml of water was shaken at room temperature for one hour. Acidification and extraction with chloroform gave 2.1 g (28%) of 3-methyl-1,2-cyclohexanedione (XVI), b.p. 69-72° (1 mm), m.p. 61-63° (from aqueous methanol). The resulting diketone (XVI) gave no depression of melting point with a known sample synthesized by the action of alkali on the dibromo derivative of 2-methylcyclohexanone (XVIII) [4].

Conversion of 2-Bromo-3-ethyl-2-cyclohexen-1-one into 3-Ethyl-1,2-cyclohexanedione. 2-Bromo-3-ethyl-2-cyclohexen-1-one (XI) (14.2 g), treated with alkali under the above-indicated conditions, gave 4.1 g (42%) of 3-ethyl-1,2-cyclohexanedione (XVII), b.p. 76-78° (1 mm), m.p. 22-23°. The substance dissolved in dilute alkali and gave a dark-violet coloration with ferric chloride.

Found %: C 68.51; 68.32; H 8.42; 8.53
$C_8H_{12}O_2$. Calculated %: C 68.6; H 8.6

*As in original – Publisher's note.

SUMMARY

Reaction of methylmagnesium iodide and of ethylmagnesium bromide with 2-bromo-1,3-cyclohexanedione (IV) gave 2-bromo-3-methyl- and 2-bromo-3-ethyl-2-cyclohexen-1-ones (X) and (XI), respectively. When these products were vacuum-distilled, they were converted into the m-substituted phenols (XII) and (XIII).

Treatment of the bromocyclohexenones (X) and (XI) with dilute alkali gave the cyclic α-diketones (XVI) and (XVII).

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SYNTHESIS AND REACTIONS OF VINYL ETHERS OF ETHANOLAMINES

COMMUNICATION 9. QUATERNARY AMMONIUM SALTS OF VINYL ETHERS OF ETHANOLAMINES

M. F. Shostakovskii and I. A. Chekulaeva

The study of the properties of products formed by reaction between vinyl ethers of ethanolamines and alkyl halides forms a natural and necessary continuation of our investigation on the reactivity of the double bonds in vinyl ethers of ethanolamines; this reactivity, as already pointed out [1-4], depends on the character of the amino group and increases as the amino hydrogens are replaced by alkyl and, particularly, by phenyl groups. Such replacement of the amino hydrogens eliminates hydrogen bonding [1, 4], while phenyl groups also have the effect of reducing the basic character of the amino group [2]. The effect of the amino group may be excluded by addition of alkyl halide at the nitrogen of these ethanolamine ethers. For investigation we took the vinyl ether of 2-diethylaminoethanol (2-vinyloxytriethylamine), the vinyl ether of 2-diphenylaminoethanol (N-2-vinyloxyethyldiphenylamine), and the trivinyl ether of triethanolamine (2,2',2"-trisvinyloxytriethylamine). We obtained the products of the addition of methyl iodide, ethyl iodide, and ethyl bromide to 2-vinyloxytriethylamine:

$$[CH_2=CHOCH_2CH_2NCH_3(C_2H_5)_2]I; \quad (I)$$

$$[CH_2=CHOCH_2CH_2N(C_2H_5)_3]I \quad (II)$$

and $[CH_2=CHOCH_2CH_2N(C_2H_5)_3]Br$. (III)

The reactions of alkyl halides with N-2-vinyloxyethyldiphenylamine and with 2,2',2"-trisvinyloxytriethylamine will be discussed below.

In the synthesis of the compounds (I), (II), and (III), reaction proceeded at room temperature at various rates. Under these conditions addition of alkyl halide at the double bond of 2-vinyloxytriethylamine was not observed, this being confirmed by hydrolysis of the reaction products with formation of acetaldehyde. The quaternary ammonium salts are readily hydrolyzed by 2% sulfuric acid with formation of acetaldehyde and the quaternary ammonium salt of 2-diethylaminoethanol in quantitative yield:

$$[CH_2=CHOCH_2CH_2NR_3]X + H_2O \rightarrow CH_3CHO + [HOCH_2CH_2NR_3]X.$$

Hydrolysis with bisulfite solution or with water proceeds much more slowly.

In the study of other reactions of the compounds (I), (II), and (III) which proceed by an ionic mechanism, we met some difficulties. We did not succeed in effecting the catalytic addition of alcohols and organic acids to the quaternary ammonium salts (I), (II), and (III), because quantitative hydrolysis occurred under these conditions. Under the influence of strong acids the quaternary ammonium salts are very readily hydrolyzed, even in presence of only traces of water, as is evidenced by the following facts: when a drop of concentrated sulfuric or hydrochloric acid is added to a solution of the quaternary ammonium salt in dry acetone, alcohol, or acetic acid, instead of the expected polymerization or addition reaction, only hydrolysis occurs. The quaternary ammonium salts do not react with alcohols when heated with them to 150°, because this reaction is preceded by decomposition of the salt in the way typical for quaternary ammonium compounds. The tendency of the quaternary salts to decompose when heated complicated their polymerization. Trials on polymerization were carried out at the melting points of the quaternary ammonium salts in presence of ferric chloride, concentrated hydrochloric

acid, or BF_3 etherate. It was found that ferric chloride did not bring about polymerization. BF_3 etherate and hydrochloric acid not only brought about polymerization but favored also other reactions (probably hydrolysis and decomposition). This peculiarity in the behavior of the quaternary ammonium salts of 2-vinyloxytriethylamine made comparison with the properties of 2-vinyloxytriethylamine itself and of unsubstituted alkyl vinyl ethers difficult.

Acylals of compounds (I) and (II) were prepared by heating them with acetic acid at 50-60°:

$$[CH_2=CHOCH_2CH_2NR_3]X + CH_3COOH \rightarrow \left[\begin{array}{l} OCOCH_3 \\ CH_3CH \\ OCH_2CH_2NR_3 \end{array}\right] X \qquad (IV)$$

The acylals (IV) are solids, and they are more difficult to hydrolyze than the acylals obtained from alkyl vinyl ethers.

Among free-radical-induced reactions we studied the polymerization of the salts (I), (II), and (III) in presence of benzoyl peroxide and of 2,2'-azobis[2-methylpropionitrile] and their copolymerization with methyl methacrylate. It was shown that the quaternary ammonium salts of 2-vinyloxytriethylamine do not polymerize in presence of these initiators (0.2% of the peroxide or 2% of the azo dinitrile; 100 hours; 60°; in ethanol solution) and may be quantitatively recovered unchanged. However, under these conditions they copolymerize with methyl methacrylate in presence of 2,2'-azobis[2-methylpropionitrile]. Work on the copolymerization will form the subject of the next paper.

N-2-Vinyloxyethyldiphenylamine $CH_2=CHOCH_2CH_2N(C_6H_5)_2$ does not react with methyl iodide, even when heated (40°).

Reaction between 2,2',2"-trisvinyloxytriethylamine and methyl iodide also proceeded at room temperature, but the immediate product $[(CH_2=CHOCH_2CH_2)_3NCH_3]I$ (V) underwent further transformations (condensation with formation of solid insoluble substances). We succeeded in isolating the quaternary ammonium salt (V) in a state approximating the monomeric form only by the strict observance of definite reaction conditions. We are probably concerned here with the polymerization of the quaternary ammonium salt under the influence of ionic catalysts (possibly products of the decomposition of methyl iodide); this indicates the high reactivity of this quaternary ammonium salt in comparison with the original 2,2',2"-trisvinyloxytriethylamine. As already noted [3], the latter does not polymerize in presence of ionic catalysts. 2,2',2"-Trisvinyloxytriethylamine reacts much more slowly with ethyl bromide than with methyl iodide, but the reaction product again undergoes spontaneous condensation.

EXPERIMENTAL*

1. Synthesis of Quaternary Ammonium Salts of 2-Vinyloxytriethylamine

a) Diethylmethyl(2-vinyloxyethyl)ammonium Iodide (I). Methyl iodide (b.p. 42-43°) (20.0 g, i.e., 0.14 mole) was added dropwise to a stirred solution of 20.0 g (0.14 mole) of 2-vinyloxytriethylamine (b.p. 155-157°; n_D^{20} 1.4325) in 25 ml of dry ether. The temperature of the reaction mixture rose slightly. The temperature was maintained at 25-30°. When addition of methyl iodide was complete, the mixture was kept for a certain time. The precipitate was filtered off, washed with dry ether, and vacuum-dried over alkali. After four hours the yield of reaction product was 19-20%, after 22 hours it was 72-74%, and after three days it was 77-80%. The quaternary ammonium salt formed colorless hydroscopic crystals, m.p. 89-90°; it was soluble in water, methanol, and ethanol, less soluble in acetone, and insoluble in benzene, dioxane, diethyl ether, butyl alcohol, heptane, cyclohexanone, and butyl vinyl ether; it yellowed after long standing.

Found %: C 38.07; 38.07; H 7.12; 7.04; N 4.56; 4.71; I 44.36; 44.27
$C_9H_{20}ONI$. Calculated %: C 37.9; H 7.06; N 4.91; I 44.5

* Laboratory Assistant B. A. Zabavina took part in the experimental work.

By reaction of 2-vinyloxytriethylamine with methyl iodide in the molar ratio of 1:2 under the same conditions we again obtained the quaternary ammonium salt (I), m.p. 89-90°; hydrolysis values found (as acetaldehyde): 99.9%, 101.2%.

The quaternary ammonium salt (I) was quantitatively hydrolyzed with 2% sulfuric acid at room temperature for 30 minutes. The acetaldehyde content was determined by the bisulfite method [5]; the hydrolysis values found were 98.9% and 98.7%. Data for hydrolysis under other conditions are given in the table.

No.	Hydrolysis conditions	Degree of hydrolysis (%)
1	Water, 100°, 5-6 hours	10-27
2	Water, 100°, 25 hours	10-19
3	Sodium bisulfite, 20°, 0.5 hour	–
4	Sodium sulfite, 20°, 3 hours	13-14

Decomposition of the quaternary ammonium salt was carried out in a distillation flask heated in Wood's alloy, the temperature of which was maintained at 220-250°. A fraction of b.p. 60-90° was distilled off; it was cloudy and had the unpleasant odor of tertiary amines. After some time, a colorless solid was precipitated; it was filtered off, washed repeatedly with acetone, and dried. It was probably a mixture of quaternary ammonium salts formed from the decomposition products; the composition of this mixture was not constant. Analytical results for two experiments:

1. Substance of m.p. 273-275°

Found %: C 35.59; 35.77; H 7.50; 7.59; I 49.90; 49.79; N 2.78; 2.62

2. Substance of m.p. 283-285°

Found %: C 35.93; 35.69; H 7.64; 7.45; I 46.70; 46.43; N 6.26; 6.31

b) Triethyl(2-vinyloxyethyl)ammonium Iodide (II). 2-Vinyloxytriethylamine (28.3 g, i.e., 0.19 mole) and 37.8 g (0.24 mole) of dry ethyl iodide (b.p. 72°) were stirred together at 16°. After one hour colorless crystals began to be precipitated. The mixture was kept for eight hours. The precipitate was filtered off, washed with dry ether, and vacuum-dried. The yield was 6.2 g (10%); m.p. 100-101°; soluble in water, methanol, and acetone.

Found %: C 40.27; 40.07; H 7.39; 7.56; N 4.83; 4.82; I 42.49; 42.48
$C_{16}H_{22}ONI$. Calculated %: C 40.14; H 7.41; N 4.68; I 42.41

Hydrolysis with 2% H_2SO_4 and subsequent determination of the acetaldehyde content by the bisulfite method gave the following results: 98.4% and 100.9%. When the filtrate had stood for six days, a further 15.3 g of product was separated; the total yield was 36.5%.

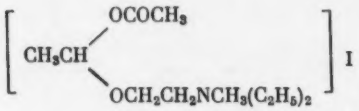
c) Triethyl(2-vinyloxyethyl)ammonium Bromide (III). A mixture of 20 g (0.14 mole) of 2-vinyloxytriethylamine and 15.3 g (0.14 mole) of ethyl bromide (b.p. 38-39°) was kept for one week at 20°. The treatment of the reaction product was similar to that used in Experiments (a) and (b). The yield of (III) was 0.9 g (2.5%). In the course of three weeks reaction had proceeded to the extent of 15%. The reaction product was a hygroscopic colorless crystalline substance, m.p. 94-95°, soluble in the same solvents as the salts (I) and (II).

Found %: C 47.19; 47.09; H 8.86; 8.75; N 5.56; 5.73; Br 31.49; 31.98
$C_{10}H_{22}ONBr$. Calculated %: C 47.62; H 8.80; N 5.55; Br 31.68

When hydrolyzed with 2% sulfuric acid it gave values of 99.2% and 98.5% (by acetaldehyde determination) for the extent of hydrolysis.

2. Reaction of the Quaternary Ammonium Salts (I) and (II) with Organic Acids

a) Reaction of the Salt (I) with Acetic Acid. A solution of 10 g (0.04 mole) of diethylmethyl(2-vinyloxyethyl)ammonium iodide (I) in 2.1 g (0.04 mole) of glacial acetic acid (in the dissolution the temperature fell from 18° to 8°) was heated at 70-80° for five hours. The dark-yellow viscous reaction mixture was dissolved in acetone. A solid was precipitated from the solution by addition of ether, and this was filtered off, purified by washing with acetone and two reprecipitations from methanol with ether, and dried. The product was a colorless solid (3.7 g), m.p. 101-102°; analysis indicated that it was the required acylal:

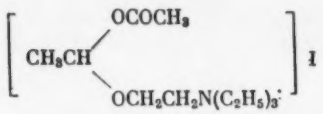


Found %: C 38.46; 38.44; H 7.07; 7.11; I 36.68; 36.64; N 3.89; 4.02
$C_{11}H_{24}O_3NI$. Calculated %: C 38.30; H 6.96; I 36.9; N 4.06

The acylal was soluble in water, methanol, and acetone, but its solubility in acetone was less than that of the original quaternary ammonium salt. This property was made use of in their separation. The acylal was hydrolyzed with water at the boil for 3-4 hours. The amounts of acetaldehyde and acetic acid formed were determined by titration (by the bisulfite method and by acidimetry, respectively). The hydrolysis values found were 98.9% and 98.2% by acid determination and 98.9% and 99.98% by acetaldehyde determination.

A further 3.1 g of the acylal, contaminated with the original ammonium salt, was isolated from the acetone-methanol-ether solution. Its hydrolysis value (by acid determination) was 88.2% (duplicate 87.2%).

b) Reaction of the Salt (II) with Acetic Acid. By reaction between 10.6 g (0.04 mole) of triethyl(2-vinyloxyethyl)ammonium iodide (II) with 2.1 g (0.04 mole) of acetic acid under similar conditions to those of Experiment (a) and similar treatment of the reaction product, we obtained 1.4 g of the acylal



and 9.5 g of a mixture of this with the original substance (acylal content of the mixture about 50%). The acylal was a colorless solid, m.p. 110-111°.

Found %: C 40.02; 39.91; H 7.23; 7.29; N 4.01; 4.06; I 35.24; 35.53
$C_{12}H_{26}O_3NI$. Calculated %: C 40.12; H 7.29; N 3.90; I 35.33

The acylal was hydrolyzed with water for four hours at the boil; the hydrolysis values obtained were 99.0% and 98.9% (acid determination) and 99.8% and 100.9% (acetaldehyde determination).

The use of excess of acetic acid, higher temperatures, and longer reaction times did not result in increased yield of acylal, but merely made purification more difficult.

3. Reaction of Quaternary Ammonium Salts of 2-Vinyloxytriethylamine with Alcohols

When a drop of concentrated hydrochloric or sulfuric acid was added to a solution of 7-8 g of the salt (I), (II), or (III) in 5-7 ml of an alcohol (methanol dried with calcium oxide, absolute ethanol, or distilled butyl alcohol), an exothermic effect (20-25°) was observed. A precipitate (6-7 g) formed, and was purified by reprecipitation from methanol with ether. In all cases this product was the corresponding quaternary ammonium salt of 2-diethylaminoethanol, which was obtained in 90-95% yield. Distillation of the filtrate gave 1.1-1.3 g of

the corresponding dialkyl acetal. The quaternary ammonium salts were colorless solids, soluble in water, methanol, and acetone.

Diethyl(2-hydroxyethyl)methylammonium Iodide (VI) $[HOCH_2CH_2NCH_3(C_2H_5)_2]I$, had m. p. 255-256°:

Found %: C 32.34; 32.09; H 7.31; 7.15; N 5.27; 5.38; I 49.74; 49.55
$C_7H_{18}ONI$. Calculated %: C 32.45; H 7.00; N 5.41; I 48.97

Triethyl(2-hydroxyethyl)ammonium Iodide (VII) $[HOCH_2CH_2N(C_2H_5)_3]I$ had m.p. 259-260°:

Found %: C 35.11; 35.24; H 7.64; 7.59; N 5.00; 5.01; I 46.56; 46.63
$C_8H_{20}ONI$. Calculated %: C 35.10; H 7.40; N 5.13; I 46.40

Triethyl(2-hydroxyethyl)ammonium Bromide (VIII) $[HOCH_2CH_2N(C_2H_5)_3]Br$ had m.p. 256-257°:

Found %: C 42.77; 42.80; H 8.95; 8.92; Br 35.16; 35.27; N 5.76; 5.87
$C_8H_{20}ONBr$. Calculated %: C 42.48; H 8.91; Br 35.33; N 6.19

The compounds (VI), (VII), and (VIII), when prepared by reaction of 2-diethylaminoethanol with the corresponding alkyl halides, had the same properties.

4. Reaction of 2,2',2"-Trisvinyloxytriethylamine with Alkyl Halides

a) A mixture of 18.9 g (0.08 mole) of the vinyl ether [b.p. 119° (4.5 mm); n_D^{19} 1.4688] and 18.5 g (0.13 mole) of methyl iodide (b.p. 42°) was kept at 15-20° for 15 hours. The reaction products were separated from unchanged reactants by vacuum evaporation at 20° and repeated reprecipitation from methanol with ether. The product was vacuum-dried at 35° (5 mm); its weight was 16.9 g. It was a light-yellow viscous liquid, soluble in water, methanol, acetone, and dioxane. Found M (cryoscopically in dioxane) 327.6; 358; calculated for $C_{13}H_{24}O_3NI$ M 369. It was evidently the quaternary ammonium salt of 2,2',2"-trisvinyloxytriethylamine (V) which had partially undergone further transformation.

Found %: C 41.32; 41.15; H 6.84; 6.44; N 3.36; 3.22; I 32.14; 32.30
$C_{13}H_{24}O_3NI$. Calculated %: C 42.3; H 6.5; N 3.8; I 34.5

It was hydrolyzed with 2% sulfuric acid at 20°. The extent of hydrolysis, as calculated from the amount of acetaldehyde formed, was 83.5% (duplicate 84.5%). After three days the molecular weight of the product had become 640 (cryoscopy in dioxane), and after three months it became much thicker and would dissolve only in methanol.

When a 2-4-fold excess of methyl iodide was taken in the reaction with 2,2',2"-trisvinyloxytriethylamine and the reaction product was not subjected to the above-described purification, the mass became solid within 24 hours and had the appearance of a transparent plate; it was broken down by water or methanol, and it darkened on standing with loss of transparency. It was insoluble in the usual organic solvents; when ground it had the appearance of rosin.

Found %: C 37.92; 37.63; H 6.33; 6.39; I 37.84; 37.18
$C_{13}H_{24}O_3NI$. Calculated %: C 42.3; H 6.5; I 34.5

b) Reaction between 20.6 g (0.09 mole) of 2,2',2"-trisvinyloxytriethylamine and 30 g (0.27 mole) of ethyl bromide at 20-25° for five months gave 4.3 g of a viscous yellow substance, which was purified by precipitation from methanol with ether; it thickened with keeping.

Found %: C 47.29; 47.18; H 7.69; 7.69; Br 23.90; 24.03; N 4.38; 4.62
$C_{14}H_{26}O_3NBr$. Calculated %: C 49.98; H 7.79; Br 23.76; N 4.16

SUMMARY

1. Quaternary ammonium salts (with CH_3I, C_2H_5I, and C_2H_5Br) of 2-diethylaminoethanol and of its vinyl ether and some related compounds were prepared and characterized.

2. Some reactions of quaternary ammonium salts of 2-vinyloxytriethylamine were investigated (hydrolysis, polymerization, reaction with alcohols and organic acids).

3. The reactions of 2,2',2"-trisvinyloxytriethylamine and of N-2-vinyloxyethyldiphenylamine with methyl iodide and with ethyl bromide were studied.

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ORGANOPHOSPHORUS POLYMERS

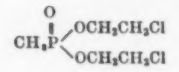
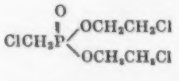
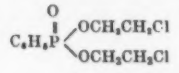
COMMUNICATION 2. POLYCONDENSATION OF BIS-2-CHLOROETHYL ALKYL- AND ARYL-PHOSPHONATES

V. V. Korshak, I. A. Gribova, and V. K. Shitikov

We discovered that, when bis-2-chloroethyl alkyl- and aryl-phosphonates are heated to 220-250°, dichloroethane is liberated and a phosphorus-containing polymer is formed. With the object of making a more detailed study of this reaction and the properties of the polymers formed, we undertook the investigation of the polycondensation of bis-2-chloroethyl methyl-, chloromethyl-, and phenyl-phosphonates, and also of tris-2-chloroethyl phosphate. These esters were obtained by reaction of the corresponding acid chlorides and 2-chloroethanol in presence of binders for hydrogen chloride [1, 2]. The properties of the esters obtained are given in Table 1.

TABLE 1

Properties of Bis-2-chloroethyl Phosphonates

No.	Formula of ester	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}
1		115—116 (1)	1.4662	1.3491
2		158—160 (3)	1.4845	1.4637
3		153—154 (1)	1.5282	1.3248

The polycondensations were carried out at 220-250°. We investigated the reaction conditions, the effect of various factors, and the thermal degradation of the polymers in detail for the case of bis-2-chloroethyl methylphosphonate. In order to determine the effect of the duration of the reaction on the amount of reaction products of low molecular weight, we carried out experiments at 220°, 230°, and 240° in which we determined the total amount of products after a certain time. We found that these products consisted in a mixture of dichloroethane, the cyclic ethylene ester of methylphosphonic acid, and unchanged bis-2-chloroethyl methylphosphonate. As will be seen from the figure, with increase in the duration of the reaction the yield of products of low molecular weight increases. Polycondensation is almost complete after 7-9 hours.

The investigation of the effect of reaction temperature on the rise in the molecular weight of the polymer and on the yield of products of low molecular weight was carried out at 220-250°, bis-2-chloroethyl methylphosphonate being heated for ten hours. The results are given in Tables 2 and 3.

TABLE 2

Effect of the Temperature of the Polycondensation of Bis-2-chloroethyl Methylphosphonate on the Molecular Weight of the Polymer

No.	Reaction temperature (°C)	Chlorine content (%)	Mol. wt. from chlorine content*	Repeating units in polymer	Yield (%)
1	220	5.3	1340	10	51.1
2	230	2.8	2539	20	58.0
3	240	1.4	5071	40	55.3
4	250	—	—	—	23.8**

* The molecular weights of the polymers were calculated from the formula: $\% Cl = \frac{71 \cdot 100}{M}$, in which % Cl is the chlorine content of the polymer (%) and M is the molecular weight of the polymer.

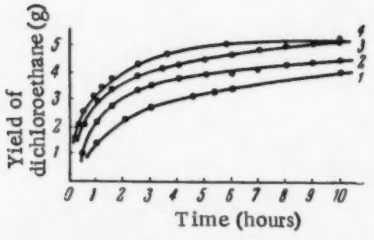
** Methylphosphonic acid was obtained. The polymer molecule decomposed with formation of methylphosphonic acid and acetaldehyde.

As can be seen from Table 2, the molecular weight of the polymer greatly depends on the reaction temperature for a given time of heating. The yield of products of low molecular weight (Table 3) is also considerably dependent on reaction temperature. Thus, the yield of low-molecular-weight products varies from 37.7% to 50.6% as the temperature rises from 220° to 250°. With rise in reaction temperature the products liberated are more readily vaporized away with a resulting shift in the equilibrium in the direction of polycondensation. When the reaction is carried out at 250°, degradation of the polymer occurs with liberation of acetaldehyde and formation of methylphosphonic acid.

TABLE 3

Amount of Low-molecular-weight Products Formed in the Polycondensation of Bis-2-chloroethyl Methylphosphonate

No.	Amount of ester taken (g)	Reaction temperature (°C)	Duration of reaction (hours)	(%) yield of low-molecular-weight products	Yield of dichloroethane (%)	Residue in flask (%)
1	15.0	220	10	37.7	27.16	10.54
2	15.0	230	10	40.6	32.32	8.28
3	15.0	240	10	43.7	36.02	7.68
4	15.0	250	10	50.6	34.40	16.20



Effect of time of heating of bis-2-chloroethyl methylphosphonate on the yield of dichloroethane at various temperatures: 1) 220°; 2) 230°; 3) 240°; 4) 250°.

In order to determine the effect of the nature of the group attached to phosphorus on the rate of polycondensation we carried out experiments with bis-2-chloroethyl methyl-, chloromethyl-, and phenyl-phosphonates and with tris-2-chloroethyl phosphate at a reaction time of ten hours. The polycondensation of bis-2-chloroethyl methyl- and chloromethyl-phosphonates was carried out at 230°. In the case of bis-2-chloroethyl phenylphosphonate the reaction did not go at 230° and it was necessary to carry it out at 250°. The polycondensation of tris-2-chloroethyl phosphate was carried out at 240° and 280°. The yield of polymer and the specific viscosity of its solution (1.5%) in cresol were determined. The results of the experiments are given in Table 4.

TABLE 4

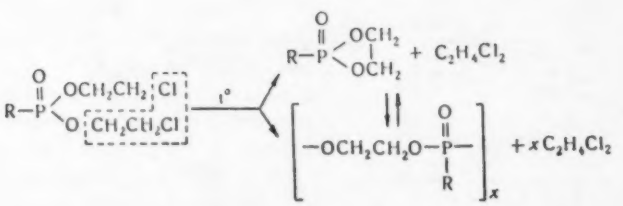
Polycondensation of Bis-2-chloroethyl Alkyl- and Aryl-phosphonates

No.	Formula of ester	Amount of ester taken (g)	Polycondensation temperature (°C)	Duration of reaction (hours)	Yield of polymer (%)	Viscosity of 1.5% solution in cresol	Total yield of low-molecular-weight products (%)	Yield of dichloroethane (%)	Residue in flask (%)
1	$CH_3P(O)(OCH_2CH_2Cl)_2$	15.0	230	10	58.0	0.08	40.6	32.3	8.3
2	$ClCH_2P(O)(OCH_2CH_2Cl)_2$	15.0	230	10	52.8	0.09	35.2	31.5	3.7
3	$C_6H_5P(O)(OCH_2CH_2Cl)_2$	15.0	250	10	62.4	0.08	33.6	31.0	2.6

As will be seen from Table 4, the nature of the substituent on phosphorus has an appreciable effect on the rate of polycondensation under given conditions. Comparing Tables 1 and 4, we may conclude that polycondensation proceeds considerably more rapidly at temperatures close to the boiling points of the respective bis-2-chloroethyl esters. The viscosity of the polymer solution does not vary appreciably with the nature of the group attached to phosphorus. The polycondensation of tris-2-chloroethyl phosphate, unlike that of bis-2-chloroethyl alkyl- and aryl-phosphonates, proceeds with copious evolution of gas after a certain interval of time, and this results in the ejection of the reaction mixture from the test tube into the receiver.

The polymers obtained were dark-colored viscous liquids, soluble in chloroform, ethanol, and cresol, but insoluble in benzene, petroleum ether, and ethyl ether. In order to estimate the thermal stability of the polymers, we carried out experiments in which the polymers were heated in a vacuum at a bath temperature of 200-220°. As a result of degradation, 3.29 g of polymer gave 1.17 g of a product of low molecular weight, b. p. 79-80° (1 mm) and n_D^{20} 1.4476; its molecular weight, determined cryoscopically in benzene, was 222. It may be supposed that the degradation of the polymer from bis-2-chloroethyl methylphosphonate proceeds in such a way that the cyclic dimer is formed. The dimer that we obtained polymerized to a mixture of tetramer and hexamer when heated in presence of about 3% of sodium at 120° for ten hours. Hence, the polymers obtained as a result of the polycondensation of these bis-2-chloroethyl esters are thermally unstable compounds.

In conclusion we must discuss briefly the possible mechanism of the polycondensation of bis-2-chloroethyl alkyl- and aryl-phosphonates, which may be represented by the following scheme:



When the bis-2-chloroethyl esters are heated, dichloroethane is eliminated and a cyclic ester is formed which, as we have shown previously [1], may polymerize. On the other hand it may be supposed that the formation of linear polymers proceeds mainly by intermolecular reaction. Also, we probably have to take into account

the existence of an equilibrium between cyclic monomer and linear polymer, such as usually exists in the polymerization of cyclic monomers.

EXPERIMENTAL

Bis-2-chloroethyl Methylphosphonate. The synthesis of bis-2-chloroethyl methylphosphonate was carried out by the method used by A. E. Arbuzov for the preparation of phosphorous esters from phosphorus trichloride and the corresponding alcohol [2]. A mixture of 161 g of 2-chloroethanol, 202 g of triethylamine, and 1800 ml of dry dioxane was prepared in a four-necked flask fitted with sealed stirrer, reflux condenser, dropping funnel, and thermometer. The mixture was cooled to below + 5°, and a solution of 133 g of methylphosphonic dichloride in 200 ml of dry dioxane was gradually added. When the addition was complete, the flask was heated for 1-1.5 hours in a boiling water bath and left to stand overnight. The precipitate of triethylamine hydrochloride was filtered off, and dioxane was distilled from the reaction mixture under reduced pressure. The bis-2-chloroethyl methylphosphonate, which remained in the flask, was vacuum-distilled; some decomposition occurred during vacuum distillation. The boiling point of the product was 115-116° (1 mm); yield 135.3 g (61.2%).

Found %: C 26.31; 26.48; H 5.03; 5.08; P 13.78; 13.87
$C_5H_{11}PO_3Cl_2$. Calculated %: C 27.14; H 5.97; P 13.98

Bis-2-chloroethyl methylphosphonate is a colorless liquid, soluble in benzene, dioxane, and diethyl ether; n_D^{20} 1.4662; d_4^{20} 1.3491; found MR 45.38; calculated MR 45.88.

The polycondensation of bis-2-chloroethyl methylphosphonate was carried out as follows: the ester (15 g) was placed in a test tube fitted with a side tube, and was heated to 220-250°. Reaction was continued for ten hours. In order to purify it the polymer was washed with benzene. The yield of polymer was 50-55%. The polymer was a brown viscous liquid and was soluble in cresol.

The low-molecular-weight products formed during the polycondensation were collected in a graduated receiver cooled with snow and were investigated. For this purpose these products were placed in a weighed flask having a side tube. The flask was heated in a boiling water bath, and a fraction was collected which had b. p. 84°; d_4^{20} 1.243; n_D^{20} 1.4443; found MR 21.12; calculated MR 21.18. These constants correspond closely with those reported for dichloroethane [3]. Vacuum fractionation of the liquid remaining in the flask gave a colorless liquid, b.p. 110-112° (2 mm); n_D^{20} 1.4590; d_4^{20} 1.3545; MR 25.18. Cryoscopic determinations in benzene gave values of 189 and 190 for the molecular weight.

Found %: C 29.87; 30.08; H 5.97; 6.00; Cl 9.63; 9.75; P 19.82; 19.80

In order to prove the presence of the cyclic ester in the mixture, the latter was polymerized in presence of about 0.5% of sodium at 120° for ten hours and at 140° for nine hours. The yield of polymer was 66.7%. The molecular weight of the polymer, as determined cryoscopically in benzene, was 662.

In order to trap acetaldehyde formed in the reaction, the outgoing gases were passed through a saturated solution of 2,4-dinitrophenylhydrazine in 2 N HCl at 0° [4]. The hydrazone precipitate formed was filtered off, washed with the original 2,4-dinitrophenylhydrazine solution, and finally washed with water until there was no reaction for chloride. The yellow crystalline solid obtained was recrystallized from alcohol and dried to constant weight at 70-80°; m.p. 149-150°.

Found %: N 24.71; 25.02
$C_8H_6N_4O_4$. Calculated %: N 25.00

A mixture test of this substance with the hydrazone obtained from acetaldehyde and 2,4-dinitrophenylhydrazine showed no depression of melting point.

In order to isolate methylphosphonic acid, the product formed in the polycondensation tube at 250° was dissolved by heating it with cresol. The solution was poured into benzene, and a white crystalline precipitate, m.p. 106°, was formed. Values of 1102.5 and 1150.7 mg of KOH per gram of substance were found for its acid value; the calculated value is 1166. The substance isolated was therefore methylphosphonic acid, obtained in 23.81% yield.

Bis-2-chloroethyl Chloromethylphosphonate. The synthesis of bis-2-chloroethyl chloromethylphosphonate was carried out by the same method [2]. The substances taken in the reaction were 2-chloroethanol (48.35 g), chloromethylphosphonic dichloride (50.0 g), triethylamine (60.70 g), and dioxane (600 ml); the yield of ester was 54.97 g (72%). The ester is a colorless liquid, b.p. 158-160° (3 mm); d_4^{20} 1.4637; n_D^{20} 1.4845; found MR 49.99; calculated MR 50.74

Found %: C 23.29; 23.54; H 4.14; 4.24
$C_5H_{10}PO_3Cl_3$. Calculated %: C 23.48; H 3.91

Bis-2-chloroethyl chloromethylphosphonate is soluble in benzene, chloroform, ether, and dioxane.

The polycondensation of bis-2-chloroethyl chloromethylphosphonate was carried out at 230°. The ester (15.1 g) was heated for ten hours. The yield of low-molecular-weight products was 5.57 g (36.2% on the original ester). Fractionation of the low-molecular-weight products gave 4.7 g (85.9% on the mixture) of dichloroethane and 0.67 g (12.2% on the mixture) of residue in the flask. The polymer obtained as a result of the reaction was purified by washing with benzene. The yield of polymer was 52.8%. The specific viscosity of a 1.5% solution in cresol was 0.09. The polymer was a dark-colored viscous liquid, readily soluble in p-cresol.

Bis-2-chloroethyl Phenylphosphonate. The substances taken in the reaction were 2-chloroethanol (61.6 g), triethylamine (77.2 g), phenylphosphonic dichloride (74.6 g), and dioxane (700 ml). The product was vacuum-fractionated, and in this process much decomposition was observed. The yield of bis-2-chloroethyl phenylphosphonate was 23.66 g (43.3%). The ester is a colorless liquid, b. p. 153-154° (1 mm); n_D^{20} 1.5282; d_4^{20} 1.3248; found MR 65.38; calculated MR 65.37

Found %: C 42.92; 42.86; H 4.68; 4.65; P 10.80; 10.75
$C_{10}H_{13}PO_3Cl_2$. Calculated %: C 42.40; H 4.59; P 10.95

The ester is soluble in dioxane, chloroform, and benzene.

The polycondensation of bis-2-chloroethyl phenylphosphonate was carried out at 250°. The ester (15 g) was heated for ten hours. The yield of low-molecular-weight products was 5.07 g (33.6% on the original ester). Fractionation of the low-molecular-weight products gave 4.64 g (91.5% on the mixture) of dichloroethane and 0.31 g (6.11% on the mixture) of residue in the flask.

The polymer formed was purified by washing with benzene. It was dried to constant weight at 60-80°; yield 62.4% (on the original ester). The molecular weight of the polymer, calculated from its chlorine content, was 5067; the number of repeating units in the polymer was 27.

Found %: C 49.84; 49.92; H 5.15; 5.09; P 15.36; 15.55; Cl 1.40; 1.39
$C_{218}H_{247}P_{27}O_{81}Cl_2$. Calculated %: C 51.63; H 4.89; P 16.51; Cl 1.40

The specific viscosity of a 1.5% solution of the polymer in cresol was 0.09. The polymer was a viscous brown liquid.

Tris-2-chloroethyl Phosphate. The synthesis of tris-2-chloroethyl phosphate was carried out by Jackson's method [5]. The substances taken in the reaction were phosphoryl chloride (72 g), 2-chloroethanol (106 g) and 250 ml of benzene. Two vacuum fractionations gave a colorless liquid, b.p. 168-170° (2 mm); n_D^{20} 1.4728; d_4^{20} 1.4289; found MR 56.07; calculated MR 57.00. The yield was 89.5 g (66.6%).

Found %: C 25.38; 25.22; H 4.14; 4.38; P 11.14; 11.11
$C_6H_{12}PO_4Cl_3$. Calculated %: C 25.21; H 4.20; P 10.85

Tris-2-chloroethyl phosphate is soluble in dioxane, benzene, chloroform, and ethanol.

The polycondensation of tris-2-chloroethyl phosphate was carried out at 240° and at 280°. Reaction proceeded with the separation of the low-molecular-weight product dichloroethane and the formation of polymer. The yield of dichloroethane varied from 28.3% to 50.9% with variation of reaction time from 4.5 to 10 hours at 240°. In the course of two hours at 280°, 25.7% of low-molecular-weight products separated. The polycondensation of tris-2-chloroethyl phosphate proceeded with copious evolution of gas, and this often resulted in ejection of the reaction mixture out of the tube into the receiver. The polymers obtained were brown viscous liquids, soluble in benzene and cresol.

SUMMARY

1. An investigation was made into the polycondensation of bis-2-chloroethyl methyl-, chloromethyl-, and phenyl-phosphonates, and also of tris-2-chloroethyl phosphate.

2. It was shown that the polycondensation of the bis-2-chloroethyl esters is accompanied by the separation of a product of low molecular weight (dichloroethane) and the formation of a polymer.

3. It was found that the polycondensation is accompanied by formation of a cyclic ester.

4. It was shown that thermal degradation of the polymer occurs at 250° with formation of methylphosphonic acid and liberation of acetaldehyde.

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HETEROCHAIN POLYAMIDES

COMMUNICATION 6. PREPARATION OF POLYAMIDES AND AMIDE-ESTER COPOLYMERS BY THE AMINOLYSIS OF POLYESTERS

V. V. Korshak, T. M. Frunze, and V. F. Petrova

By the study of several typical examples we have shown that heterochain macromolecular compounds are able to undergo various exchange reactions under the action of the original low-molecular-weight reactants [1]. Korshak and Golubev [2] studied the acidolysis of polyesters under the action of adipic acid, and Korshak and Vinogradova [3, 4] studied the alcoholysis of polyesters when heated with hexadecyl alcohol, and also their esterolysis when heated with esters. The aminolysis of a polyester, which has not yet been described in the literature, would be a reaction of this sort. This reaction is of interest not only as a process characterizing the chemical properties of polyesters, but as a route to the preparation of amide-ester copolymers and polyamides. We therefore investigated this reaction.

EXPERIMENTAL

The polyester studied was obtained by the polycondensation of ethylene glycol with dimethyl sebacate in presence of 0.25% of lithium hydroxide. It melted at 70-73°, and its molecular weight, as determined from the viscosity of a 0.5% solution in benzene, was about 9000 (specific viscosity 0.24; $K_{equiv} = 0.93 \cdot 10^{-4}$). The reaction between polyethylene sebacate and 1,6-hexanediamine was carried out under the following conditions: the reaction mixture was heated in a test tube in an atmosphere of nitrogen at 150° for 0.5 hour, at 180° for 1 hour, at 200° for 1 hour, at 220° for 1 hour, at 250° for 1 hour, and then at 250° for 3 hours at a residual pressure of 1-2 mm. Mixtures of polyester and 1,6-hexanediamine containing 10-100 moles percent of polyester were treated in this way. The melting points and viscosities (as 0.5% solution in cresol) of the products were determined. The results are given in Table 1.

TABLE 1

No.	Amounts of original components (moles)		Melting point of polymer obtained (°C)	Specific viscosity of 0.5% solution in cresol	Degree of polymerization (X)
	Polyester	1,6-Hexanediamine			
1	1	1.0	225—230	0.35	32
2	1	0.9	203—206	—	—
3	1	0.8	200—203	0.35	37
4	1	0.7	199—202	—	—
5	1	0.6	190—198	0.26	29
6	1	0.5	180—182	0.26	25
7	1	0.4	175—178	0.18	21
8	1	0.3	170—175	0.37	44
9	1	0.2	147—255	0.27	33
10	1	0.1	120—123	—	—
11	1	0.0	70—73	0.26	41

The products were light-yellow opaque solids; they were readily soluble in cresol. Some of them, namely polymers obtained with 10 and 20 moles percent of 1,6-hexanediamine, were completely soluble in hot benzene. The products obtained with 30-80 moles percent of 1,6-hexanediamine were only partly soluble in hot benzene. The products prepared with a still higher proportion of 1,6-hexanediamine were completely insoluble in benzene. The products obtained with a large proportion of 1,6-hexanediamine were horny substances. Reduction in the proportion of 1,6-hexanediamine had the result that the properties of the products approximated more and more to those of the original polyester.

By treatment with hot benzene some of the products were separated into two parts: benzene-soluble and benzene-insoluble fractions. Table 2 gives the characteristics of the unfractionated products and of the benzene-soluble and benzene-insoluble fractions.

TABLE 2

No.	Amount of 1,6-hexanediamine (moles %)	Unfractionated product			Products obtained after extraction			
					Benzene-insoluble residue		Benzene-soluble part	
		M.p. (°C)	Nitrogen content (%) ·		M.p. (°C)	nitrogen content (%)	M.p. (°C)	nitrogen content (%)
			found	calculated				
1	100	225—230	9.30	9.92	225—230	9.35	—	—
2	40	175—178	3.74	4.23	184—190	3.60	70—73	0.0
3	20	147—155	2.27	2.16	—	—	130—135	2.97
4	10	120—123	1.51	1.09	—	—	106—118	1.05

As will be seen from Table 2, with reduction in the 1,6-hexanediamine content the amount of benzene-insoluble fraction diminishes. Products with a medium 1,6-hexanediamine content consist of two parts: benzene-insoluble and benzene-soluble parts having different nitrogen contents.

DISCUSSION OF RESULTS

The reaction between the polyester and 1,6-hexanediamine is an example of aminolysis, which proceeds between equivalent amounts of the reactants in accordance with the equation:

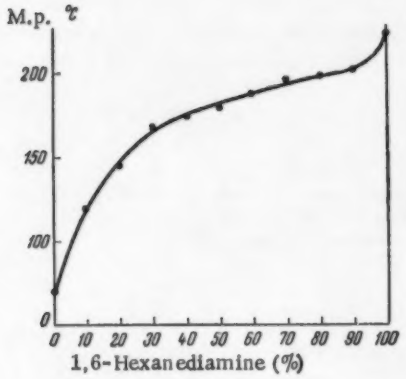
$$HO(CH_2)_2O[CO(CH_2)_8COO(CH_2)_2O-]_xH + (x+1)H_2N(CH_2)_6NH_2 \rightarrow H_2N(CH_2)_6NH-$$
$$-[-CO(CH_2)_8CONH(CH_2)_6NH-]_x-H + (x+1)HO(CH_2)_2OH$$

Hence, when there is 1 mole of 1,6-hexanediamine to 1 basal mole of polyester, the reaction should result in the formation of hexamethylenesebacamide, and this does in fact occur. This reaction, therefore, provides a new method for the preparation of polyamides. When it is carried out with smaller amounts of 1,6-hexanediamine, the products are amide-ester copolymers, whose properties depend on the amount of 1,6-hexanediamine taken for reaction, as can be seen from the results of the investigation of the products. In this reaction ethylene glycol is liberated and, owing to its volatility, is readily removed from the sphere of reaction. With change in the amount of 1,6-hexanediamine taken for reaction, the melting point of the product varies in the way shown in the graph.

It will be seen from the figure that there is a smooth change in melting point with increase in the amount of 1,6-hexanediamine taken for reaction. There is a particularly sharp rise in melting point at the beginning (small amounts of 1,6-hexanediamine). In the middle part of the graph the melting point rises rather slowly.

Reaction results in the formation of amide-ester copolymers, whose formation in the case of reaction 0.5 mole of 1,6-hexanediamine and 1 basal mole of polyester can be expressed as follows:

$$[-CO(CH_2)_8COO(CH_2)_2O-]_x + {}^1/_2xH_2N(CH_2)_6NH_2 \rightarrow$$
$$\rightarrow [-CO(CH_2)_8COO(CH_2)_2OCO(CH_2)_8CONH(CH_2)_6NH-]_{x/2} + {}^1/_2x\,HO(CH_2)_2OH\,.$$



The reaction that we are considering consists in the aminolysis of the polyester under the action of 1,6-hexanediamine. The elementary reaction will be the breaking of the ester linkage under the attack of an amino group:

$$\cdots -O(CH_2)_2O-CO(CH_2)_8CO-\cdots + H_2N(CH_2)_6NH_2 \rightarrow$$
$$\rightarrow \cdots -O(CH_2)_2OH + H_2N(CH_2)_6NHCO(CH_2)_8CO-\cdots$$

Depending on the amount of 1,6-hexanediamine taken, a greater or smaller number of ester linkages are broken. It is difficult to suppose that the 1,6-hexanediamine molecule displaces a whole ethylene glycol molecule in a single act and takes its place. It is clearly more probable that a greater or smaller number of fragments are formed having hydroxy or amino end groups. These fragments will then react further among themselves with formation of the final macromolecule:

$$\cdots -CO(CH_2)_8CO-O(CH_2)_2OH + H_2N(CH_2)_6NHCO(CH_2)_8CO-\cdots \rightarrow$$
$$\rightarrow \cdots -CO(CH_2)_8CO-NH(CH_2)_6NHCO(CH_2)_8CO-\cdots + HO(CH_2)OH.$$

It is clear that the molecular weight of the amide-ester copolymer or polyamide obtained depends mainly on the conditions under which the last stage of the reaction is carried out and is not directly related to the molecular weight of the original polyester. This view is confirmed by the variation in the degrees of polymerization of the reaction products, which are given in the last column of Table 1. There is no regularity to be observed in the variation of the degree of polymerization; this is independent of the amount of diamine taken.

SUMMARY

The aminolysis of polyethylene sebacate with 1,6-hexanediamine was investigated and it was found that exchange of ethylene glycol and 1,6-hexanediamine residues occurs with formation of amide-ester copolymers or polyamides, depending on the relative amounts of reactants.

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* In Russian.

HETEROCHAIN POLYAMIDES

COMMUNICATION 7. THERMODEGRADATION OF POLYHEXAMETHYLENEADIPAMIDE

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The great extension of the fields of application of high polymers in recent years has made it necessary to study their behavior under various conditions of use and storage; this includes the study of aging phenomena. In order to assess the serviceability properties of a polymer it is extremely important to understand the processes taking place during aging and the factors that cause aging; the causes and consequences of aging differ for different polymers.

The aging of polymers may be due to various external causes, both physical (light and various forms of high-energy radiation, heat, mechanical action, etc.) and chemical. Each of these factors may bring about both purely physical changes in the polymer (loss of volatile components, change in degree of crystallinity, change in relaxation properties, etc.) and also changes in chemical structure (above all, breaking of chemical bonds with formation of free radicals which induce various secondary degradation and cross-linking processes, which may proceed with or without the participation of oxygen [1]). The elucidation of these matters would make is possible to make more accurate predictions of the behavior of materials under conditions of use and to find means of protecting polymers from aging.

In view of the enormous variety of aging phenomena [2, 3], it was considered to be expedient to make a more detailed investigation of one of the simplest cases of aging, namely thermal aging.

As the object for investigation we selected a polyamide, namely polyhexamethyleneadipamide. We naturally turned our attention first to the effect of heating the fused polyamide on its molecular weight. This question is of interest, for it is known from the literature that polyamides are degraded at high temperatures with separation of products of low molecular weight [4, 5] and are capable, under certain conditions, of undergoing interchain-exchange reactions [6-10].

EXPERIMENTAL*

The polyamides used in this investigation were products of the polycondensation of adipic acid with 1,6-hexanediamine and differed from one another in molecular weight. Three samples were studied: a commercial sample of molecular weight 18,000 (stabilized with acetic acid) and two unstabilized samples of molecular weights 35,000 and 55,000, prepared specially in the laboratory in the following way. 1,6-Hexanediamine adipate, which had been recrystallized from 80% ethanol and had m.p. 191.5°, was placed in a glass tube, which, after repeated purges with pure nitrogen, was sealed under vacuum. The sealed tube was heated in an oil bath at 270-275° for three hours. When cool, the contents of the tube were transferred to the reaction test tube, and heating was continued in a stream of nitrogen (2 hours at 275° without vacuum and not less than 6 hours in a vacuum). The polyamide of molecular weight 35,000 was obtained by heating the mass in a vacuum for six hours, and that of molecular weight 55,000, by heating the mass in a vacuum for eight hours.

All three polyamide samples were heated in a stream of nitrogen above the melting point. In this way we determined the effect of heating on polyamides of identical composition and structure, but different molecular weight. The heating was carried out in a glass test tube (in which 5 g of polyamide was placed) immersed in Wood's alloy and heated to the necessary temperature in a stream of nitrogen. The time of heating was varied

* Senior laboratory assistant V. E. Sheina took part in this work.

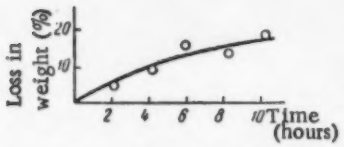

Fig. 1. Relation of loss in weight of polyamide to time of heating at 300°

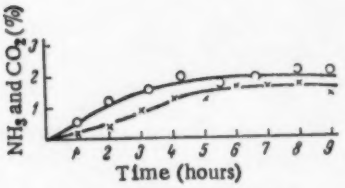

Fig. 2. Relation of amount of CO_2 and NH_3 (or amines) liberated from the polyamide at 300° to the time of heating.

from 30 minutes to 12 hours. The nitrogen leaving the tube passed through a system of absorbers in order to trap the gases liberated in the heating.

For the trapping of gaseous products liberated in the heating of the polyamide we used 0.1 N HCl and 50% KOH; these had the purpose of binding the CO_2, NH_3, and amines liberated.

The changes in the polyamide resulting from heating were determined by viscosity measurements on 0.5% solutions of the polyamides in m-cresol before and after the heat treatment and also from the change in weight of the sample. The molecular weight M of the polyamide was calculated [11] by the formula

$$\left(\frac{\eta_{sp}}{c}\right) = 0{,}522 \cdot 10^{-4} \; M^{1{,}26},$$ in which $\underline{c}$ = 5 g/liter.

The most detailed investigation was carried out on the polyamide of molecular weight 18,000.

Fig. 1 shows the relation of the loss in weight of the polyamide sample to the time of heating at 300 ± 5°.

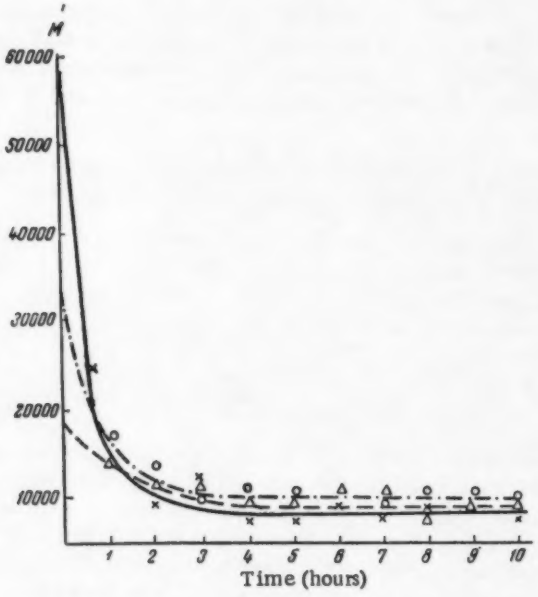

Fig. 3. Relation of the molecular weight of the polyamide to the time of heating at 300° (in a stream of nitrogen). Initial molecular weight: × – 55,000; O – 35,000; Δ – 18,000.

Figure 2 shows the time-dependence of the amounts of CO_2 and NH_3 (or amines) liberated during the heating of a sample of polyamide of molecular weight 18,000. The changes in the molecular weights of the three samples of polyamide during heating at 300 ± 5° in a stream of nitrogen can be followed from Fig. 3.

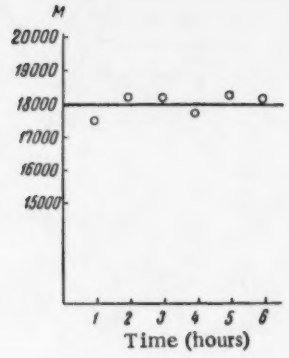

Fig. 4. Relation of the molecular weight of the polyamide (initial molecular weight 18,000) to the time of heating at 270° (in a stream of nitrogen).

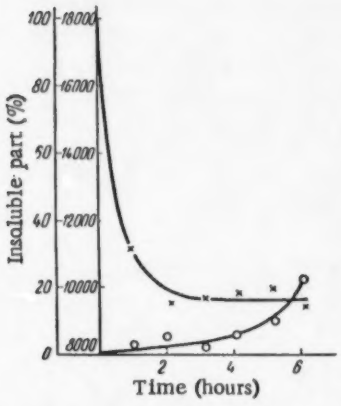

Fig. 5. Relation of the content of the insoluble part and of the molecular weight of the soluble part of the polyamide to the time of heating at 300° in a stream of air: O – insoluble part (%); × – molecular weight of the soluble part.

It will be seen from Fig. 3 that, when the three samples of different molecular weights have been heated for four hours, constancy of molecular weight is established and the values are the same for all three samples (about 9000). The establishment of a definite molecular weight was confirmed also by similar experiments at 270 ± 5° in a stream of nitrogen on a sample of polyamide of molecular weight 18,000. The results of these measurements are given in Fig. 4. It is interesting to note that the difference in the end groups of the investigated samples had no effect on the value assumed by the molecular weight after heating. However, this value depends on the temperature at which equilibrium is established. It was noted that heating of the polyamide at 330 ± 5° results not only in reduction in the molecular weight of the soluble part, but also in the formation of a cresol-insoluble substance, the amount of which increases with increase in the duration of heating (after six hours of heating the insoluble part amounted to 97%).

The polyamide of molecular weight 18,000 was also heated in a stream of air at 300 ± 5°, the air being drawn through the heated polymer at the rate of one bubble per second. The formation of a cresol-insoluble part was again observed, the amount formed increasing as heating continued; there was a simultaneous fall in the molecular weight of the soluble part (Fig. 5).

DISCUSSION OF RESULTS

Examination of Fig. 3 shows that in the course of isothermal heating there is a fall in molecular weight resulting in the establishment of a quite definite value (about 9000 at 300°) which is independent of the molecular weight and end groups of the original polymer. Consequently, thermal degradation of the polyamide in the inert medium is accompanied by processes of chain growth. However, at the start of the heating degradation definitely predominates. In principle, degradation can proceed at the ends of the polymer chain and also at any intermediate point. In our case fall in molecular weight proceeds irrespective of the type of end groups and is more pronounced for polyamides of high molecular weight, so that it can readily be inferred that degradative acts occur not only at the ends of chains, but also at any place in the chains, probably at any amide linkage.

The position may be illustrated as follows. It is known [12] that the introduction of a definite amount of degrading agent results in a fall in the molecular weights of polyamides of various degrees of polymerization (Table 1). In our case the number of degradative acts is determined by the time of heating (Table 2). Comparison of the results given in Tables 1 and 2 and in Figs. 6-8 shows quite clearly that, at first, our experimentally-found change in the molecular weights of polyamides during heating corresponds in general character to the course of degradation calculated from the formula given by Korshak [12], but differs from this in that after a time the fall in molecular weight ceases. The leveling of the values of the molecular weights shows that in our case the degradation of the polyamide molecules proceeds independently of their molecular weights, i.e., independently of the number and character of the end groups.

TABLE 1

Amount of degrading agent	Calculated values*				
	Degree of polymerization			$\frac{X_2}{X_1}$	$\frac{X_3}{X_1}$
	X_1, (initial mol. wt. 18,000)	X_2, (initial mol. wt. 35,000)	X_3, (initial mol. wt. 55,000)		
0.0	80	155	245	1.94	3.06
1.0	44.7	61.0	71.2	1.36	1.59
2.0	31.0	38.0	41.7	1.22	1.35
3.0	23.8	27.6	29.4	1.16	1.23
4.0	19.3	21.6	22.8	1.12	1.18
6.0	13.9	15.1	15.6	1.09	1.12
8.0	10.9	11.6	11.9	1.06	1.09

* The calculation was carried out by the formula:

$$X = \frac{X_0}{(X_0 - 1)\,q/100 + 1},$$

in which X is the degree of polymerization after degradation; X_0 is the original degree of polymerization; q is the amount of degrading agent (moles %); and $X_0 - 1$ is the number of linkages in the original polymer molecule at which degradation can occur.

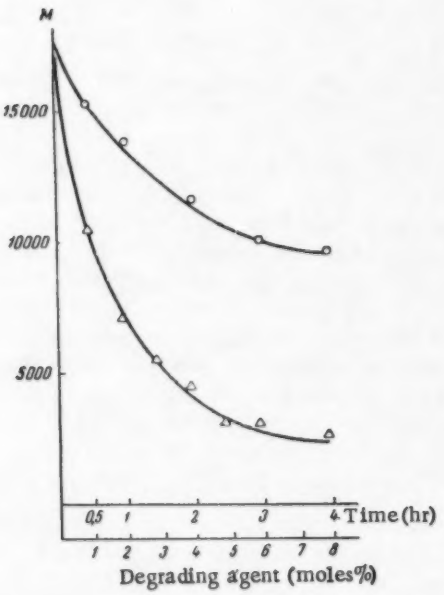

Fig. 6. Experimental relation of the molecular weight of the polyamide (initial molecular weight 18,000) to the time of heating at 300° in a stream of nitrogen (O), and the theoretical relation of the molecular weight to the amount of added degrading agent (Δ).

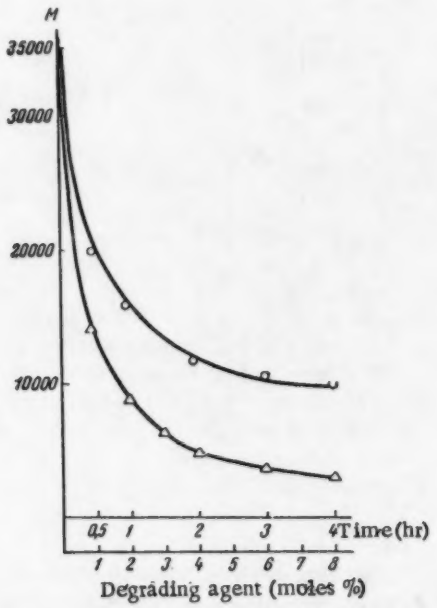

Fig. 7. Experimental relation of the molecular weight of the polyamide (initial molecular weight 35,000) to the time of heating at 300° in a stream of nitrogen (O), and the theoretical relation of the molecular weight to the amount of added degrading agent (Δ).

TABLE 2

Time of heating at 300° (hours)	Experimental results: Degree of polymerization X_1 (initial mol. wt. 18,000)	X_2 (initial mol. wt. 35,000)	X_3 (initial mol. wt. 55,000)	$\frac{X_2}{X_1}$	$\frac{X_3}{X_1}$
0.0	80	155	245	1.94	3.02
0.5	66	88	115	1.33	1.73
1.0	60	71	66.5	1.19	1.11
—	—	—	—	—	—
2.0	51	53	46	1.05	0.91
3	44	46	42	1.05	0.95
4	42	44	40	1.05	0.95

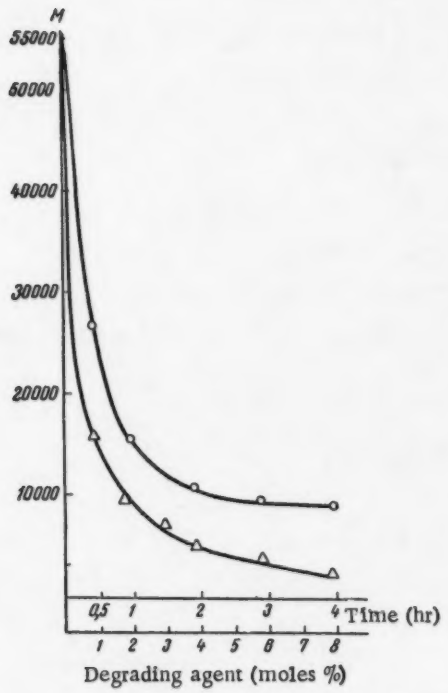

Fig. 8. Experimental relation of the molecular weight of the polyamide (initial molecular weight 55,000) to the time of heating at 300° in a stream of nitrogen (O), and the theoretical relation of the molecular weight to the amount of added degrading agent (Δ).

This breakdown process is distinguished clearly only in the initial stage, when the molecular weights are high; in the course of time it is distorted by the ever-increasing effect of cross-linking processes, as a result of which constant molecular weight is established despite the continuing degrading effect of temperature. In the heating of the polyamide at 330°, the cross-linking process predominates over degradation and results in the formation of an insoluble polymer.

In the second stage, therefore, when equilibrium has already been established, balanced processes of chain breakdown at an arbitrary repeating unit and of combination of colliding molecules into one molecule proceed in the polyamide. Hence, the results reported here on changes in the molecular weights of polyamides during heating confirm once more that degradative and interchain exchange reactions proceed in these polymers and, at a given temperature, result in the establishment of a dynamic equilibrium.

Apart from the above-described processes, in the heating of polyamides there occur also other irreversible chemical changes, which result in the formation of branched and three-dimensional structures. These occur during heating at higher temperatures (330°), at which an insoluble fraction is formed even in an inert medium, and also during prolonged heating at 270°.

In connection with this work further investigation is required into the concrete mechanisms of all these processes and also into the possibility of their occurrence in the solid phase, i. e., in fibers, films, and masses. In the investigation of the aging of polyamide materials it is of great importance to study changes of molecular weight in solid polyamides under the action of mechanical treatments and also of combinations of deformations, heat, and light both in inert media and in presence of oxygen, which has a considerable cross-linking effect (Fig. 5).

SUMMARY

1. The effect of heating polyhexamethyleneadipamide in an inert medium on its molecular weight was investigated, and it was shown that, irrespective of the initial degree of polymerization, a definite value of the

molecular weight is established in the fused polyamide, this value being dependent on the temperature at which the polyamide is heated.

2. The nature of the end groups of the polyamide does not appear to affect the establishment of the equilibrium molecular weight during heating in an inert medium.

3. Emphasis is placed on the part played by degradation-recombination equilibria, in particular by interchain exchange reactions, in the establishment of the equilibrium value of the molecular weight of the polyamide under the conditions indicated.

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*In Russian.

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CARBON-CHAIN POLYMERS AND COPOLYMERS

COMMUNICATION 1. SYNTHESIS AND POLYMERIZATION OF p-ALKOXYSTYRENES

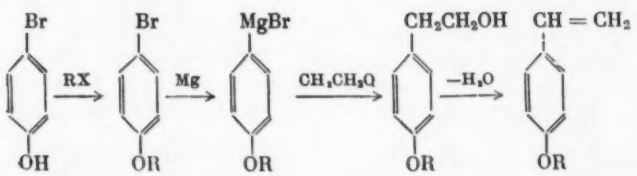
G. S. Kolesnikov and G. M. Pogosian

The elucidation of the relationship between the structures of macromolecular compounds and their properties forms one of the main tasks of the chemistry of such compounds, and many investigations have been devoted to this question. One characteristic of macromolecular compounds is the glass transition temperature, but there is no uniform way of determining this constant and it is difficult to compare results obtained by different investigators.

The effect of the size of the alkyl group of p-alkylstyrenes on the glass temperature of the polymers was studied for n-alkyls by Overberger and co-workers [1]. These investigators found that, as the length of the alkyl radical was increased, the glass temperature of the polymer fell, attaining a minimum value for a C_{10} alkyl; further lengthening of the alkyl radical resulted in a rise in the glass temperature. The authors offer no explanation for this phenomenon; in our opinion, the rise in glass temperature with lengthening of the alkyl radical (beyond C_{10}) is a consequence of the occurrence of crystallization in a system of long alkyl radicals. A similar picture was observed in a study of the effect of the size of the alkyl radical on the brittle point of polymers of n-alkyl acrylates and methacrylates [2, 3]: for polyacrylic esters the minimum brittle point was found for C_8, and for polymethacrylic esters it was found for C_{12}.

We considered that it would be of interest to determine the effect of the size of an alkoxy group in the p-position to a vinyl group on the glass point of poly-p-alkoxystyrenes, for the introduction of an oxygen atom between the aromatic nucleus and the alkyl radical should affect the properties of the polymer, including the glass point. With this object we undertook the synthesis of various p-alkoxystyrenes, polymerized them, and determined the glass points of the reprecipitated polymers. The determination of glass points of reprecipitated polymers was more accurate than that of samples of block polymers, because the latter may contain some unchanged monomer and impurities present in the original monomer; this unchanged monomer and the impurities would plasticize the polymer formed, which would result in lowering of the glass point. The glass points were determined in the apparatus designed by Tsetlin and co-workers [4] for the measurement of this temperature for macromolecular substances in powder form.*

p-Alkoxystyrenes were synthesized as follows:



They were polymerized in presence of 0.75 moles percent of benzoyl peroxide at 40-120°, heating being continued until a solid block or highly viscous liquid was formed. The polymers were reprecipitated by slowly

* The authors express their thanks to B. L. Tsetlin for the determination of the glass points of poly-p-alkoxystyrenes.

introducing a 2% solution of the polymer in benzene or dichloroethane into methanol with stirring; the reprecipitated polymer was dried to constant weight at 50°. The results are given in the table.

p-Alkoxystyrenes

Alkoxystyrene	Yield (%)	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	Glass point (°C)
p-Methoxystyrene	46.5	85—87 (12)	1.0038	1.5618	89
p-Ethoxystyrene	45.0	99—100 (11)	0.9940	1.5475	86
p-Propoxystyrene	41.3	110—111 (13)	0.9710	1.5422	70
p-Butoxystyrene	48.5	129—130 (14) 156—157 (45)	0.9533	1.5354	47
p-Isopentylstyrene	29.0	161—163 (45)	0.9800	1.5252	57

It will be seen from the table that in the series of p-n-alkoxystyrenes the glass point falls with increase in the length of the aliphatic radical of the alkoxy group. x-Ray structure analysis showed that all the poly-p-alkoxystyrenes obtained were amorphous.* Comparison with the glass points of poly-4-n-alkylstyrenes [1] showed that, for a given number of carbon atoms in the p-substituent, the glass point of the poly-p-alkoxystyrene was the higher. Thus, the glass points of poly-p-ethylstyrene and poly-p-ethoxystyrene are 27° and 86°, and those of poly-p-butylstyrene and poly-p-butoxystyrene are 6° and 47°, respectively. It is quite obvious that the higher glass temperatures of poly-p-alkoxystyrenes are to be attributed to the presence of an oxygen atom between the aromatic nucleus and the alkyl radical. It may be supposed that, owing to the presence of an oxygen atom, hydrogen bonds may be formed (at the expense of hydrogen atoms of the aromatic nucleus) between polymer molecules, which must result in closer packing of polymer chains and hence to a rise in the glass point of the polymer.

EXPERIMENTAL

p-Methoxystyrene

p-Bromoanisole. a) Preparation of p-bromoanisole from anisole [5]. A mixture of 108 g of anisole and 108 g of glacial acetic acid was prepared in a flask fitted with stirrer, reflux condenser, and dropping funnel and was cooled in an ice-salt mixture while 160 g of bromine was added dropwise. When the evolution of hydrogen bromide had become insignificant, the reaction mixture was poured into water. The organic layer was separated, washed two or three times with water, dried with calcium chloride, and distilled. A fraction of b.p. 216-223° was collected, and redistillation of this under reduced pressure gave 103 g (55%) of p-bromoanisole, b.p. 100-102° (12 mm).

b) Preparation from p-bromophenol. p-Bromophenol (173 g) was placed in a flask fitted with stirrer, reflux condenser, and dropping funnel, and a solution of 56 g of potassium hydroxide in 200 ml of alcohol was added. When the p-bromophenol had dissolved, 170.4 g of methyl iodide was added, and the mixture was stirred at a gentle boil in a water bath for 6-8 hours. The reflux condenser was replaced by one set for distillation, stirring was stopped, and alcohol was distilled off. A small amount of water was added to the residue, and the organic layer was separated. The aqueous layer was extracted twice with ether, and the ether extracts were combined with the organic layer. This was washed with 50 ml of 10% sodium hydroxide solution and dried with calcium chloride; ether was distilled off. Distillation gave 158 g (84.5%) of p-bromoanisole, b.p. 220-223°.

p-Methoxyphenethyl Alcohol. An organomagnesium compound was prepared from 187 g of p-bromoanisole and 24 g of magnesium turnings in 450 ml of dry ether. The solution was cooled with ice and salt, and a cooled solution of 52 g of ethylene oxide in 150 ml of ether was added dropwise; cooling was discontinued, and the contents of the flask were boiled for one hour. The organomagnesium compound was decomposed with a 3-5% solution of acetic acid or a saturated solution of ammonium chloride, and the ether layer was separated,

* The x-ray structure analysis of polymers was carried out in the x-Ray Structure Analysis Laboratory by Iu. T. Struchkov, to whom we express our sincere thanks.

washed 2-3 times with water, and dried with magnesium sulfate or sodium sulfate; ether was distilled off, and the residue was vacuum-distilled. The fraction collected, b.p. 157-159° (19 mm) and m.p. 22-23°, amounted to 82 g (54%).

Its phenylurethan had m.p. 123-124° (from alcohol).

Found %: C 70.35; 70.47; H 6.71; 6.51; N 5.12; 5.21
$C_{16}H_{17}NO_3$. Calculated %: C 70.83; H 6.31; N 5.16

p-Methoxystyrene. A mixture of 36.4 g of potassium hydroxide, 2 g of hydroquinone, and 76 g of p-methoxyphenethyl alcohol was prepared in a Claisen flask and was heated at a pressure of 10-15 mm in a bath of Wood's alloy at 220-230°. The reaction products were condensed in a condenser, 100 ml of ether was added to the condensate, and the ethereal solution was washed three times with 10% sodium hydroxide solution and then with water until the reaction was neutral. Water was separated carefully, the ethereal solution was dried with calcium chloride, ether was distilled off, and vacuum distillation of the residue gave 31.2 g (46.5%) of a fraction of b.p. 85-87° (12 mm).

p-Ethoxystyrene

p-Bromophenetole was prepared in the same way as p-bromoanisole. Reaction between 122 g of phenetole and 160 g of bromine in 122 g of glacial acetic acid gave 116.6 g (58%) of p-bromophenetole, b.p. 227-233° or 100-103° (5 mm). Reaction between 173 g of p-bromophenol, 56 g of potassium hydroxide, and 130.8 g of ethyl bromide in 200 ml of alcohol gave 181 g (81%) of p-bromophenetole, b.p. 224-225°.

p-Ethoxyphenethyl Alcohol was prepared in the same way as p-methoxyphenethyl alcohol from 201 g of p-bromophenetole, 24 g of magnesium, and 52 g of ethylene oxide; yield 77.2 g (46.5%); b.p. 175-180° (30 mm); m. p. 39-40°.

p-Ethoxystyrene was prepared by the dehydration of p-ethoxyphenethyl alcohol with the aid of 36.5 g of potassium hydroxide in presence of 2 g of hydroquinone. The yield of p-ethoxystyrene, b. p. 99-100° (11 mm), was 33.3 g (45%).

p-Propoxystyrene

Phenyl Propyl Ether [5]. Phenol (94 g) and a solution of 56 g of potassium hydroxide in 200 ml of alcohol were placed in a flask fitted with stirrer, reflux condenser, and dropping funnel. When the phenol had dissolved, 135.3 g of propyl bromide was added, and the mixture was heated in a water bath with stirring for 5-6 hours in such a way that it boiled gently. The reflux condenser was replaced by one set for distillation, and the mixture was stirred while ethanol was distilled off. A little water was added to the residue, and the organic layer was separated. The aqueous layer was extracted twice with ether, and the ethereal solutions were combined with the organic layer, which was washed with 50 ml of 10% sodium hydroxide solution and dried with calcium chloride; ether was distilled off. Distillation of the residue gave 123.7 g (90.9%) of phenyl propyl ether, b. p. 187-190°.

p-Bromophenyl Propyl Ether was prepared in the same way as p-bromoanisole. Bromination of 136 g of phenyl propyl ether in 136 g of glacial acetic acid with 160 g of bromine gave 124.7 g (58%) of p-bromophenyl propyl ether, b.p. 238-240° or 117-120° (13 mm). Reaction between 173 g of p-bromophenol, 56 g of potassium hydroxide, and 135.3 g of propyl bromide in 200 ml of alcohol gave 189.2 g (88%) of p-bromophenyl propyl ether.

p-Propoxyphenethyl Alcohol was prepared in the same way as p-methoxyphenethyl alcohol. Reaction between 215 g of p-bromophenyl propyl ether, 24 g of magnesium, and 52 g of ethylene oxide gave 85.6 g (47%) of p-propoxyphenethyl alcohol, b.p. 157-160° (11 mm) and m.p. 38-39°.

Its phenylurethan had m.p. 105-106° (from alcohol).

Found %: C 72.08; 72.12; H 7.06; 7.03; N 4.93; 4.71
$C_{18}H_{21}NO_3$. Calculated %: C 72.55; H 7.10; N 4.67

p-Propoxystyrene was prepared in the same way as p-methoxystyrene by the dehydration of 84.6 g of p-propoxyphenethyl alcohol with the aid of 37.5 g of potassium hydroxide in presence of 1 g of hydroquinone; yield 31.4 g (41.3%); b. p. 110-111° (13 mm).

p-Butoxystyrene

Butyl Phenyl Ether was prepared in the same way as phenyl propyl ether. Reaction between 94 g of phenol, 56 g of potassium hydroxide, and 137 g of butyl bromide in 200 ml of alcohol gave 136.5 g of butyl phenyl ether, b.p. 207-210°; yield 91%.

p-Bromophenyl Butyl Ether was prepared in the same way as p-bromoanisole. Bromination of 150 g of butyl phenyl ether in 150 g of glacial acetic acid with 160 g of bromine gave 103.5 g (45.2%) of p-bromophenyl butyl ether, b. p. 258-260° or 127-130° (9 mm). Reaction between 173 g of p-bromophenol, 56 g of potassium hydroxide, and 137 g of butyl bromide in 200 ml of alcohol gave 192.4 g (84%) of p-bromophenyl butyl ether.

p-Butoxyphenethyl Alcohol was prepared in the same way as p-methoxyphenethyl alcohol. Reaction between 229 g of p-bromophenyl butyl ether, 24 g of magnesium, and 52 g of ethylene oxide gave 84.4 g (43.5%) of p-butoxyphenethyl alcohol, b.p. 174-176° (16-17 mm) and m.p. 32-33°.

Its phenylurethan had m.p. 98-99° (from alcohol).

Found %: C 73.22; 73.15; H 7.52; 7.46; N 4.34; 4.23
$C_{19}H_{23}NO_3$. Calculated %: C 72.81; H 7.39; N 4.49

p-Butoxystyrene was prepared in the same way as p-methoxystyrene by the dehydration of 48.5 g of p-butoxyphenethyl alcohol with the aid of 18.2 g of potassium hydroxide in presence of 1 g of hydroquinone; the yield of p-butoxystyrene was 21.4 g (48.5%); b. p. 129-130° (14 mm).

p-Isopentyloxystyrene

Isopentyl Phenyl Ether was prepared in the same way as phenyl propyl ether. Reaction between 94 g of phenol, 56 g of potassium hydroxide, and 151 g of isopentyl bromide in 200 ml of alcohol gave 153.3 g (93.5%) of isopentyl phenyl ether, b. p. 221-225°.

p-Bromophenyl Isopentyl Ether was prepared in the same way as p-bromoanisole. Bromination of 164 g of isopentyl phenyl ether with 160 g of bromine in 164 ml of glacial acetic acid gave 102 g (42%) of p-bromophenyl isopentyl ether, b. p. 148-150° (20 mm). Reaction between 173 g of p-bromophenol, 56 g of potassium hydroxide, and 151 g of isopentyl bromide in 200 ml of alcohol gave 183.7 g (75.6%) of p-bromophenyl isopentyl ether.

p-Isopentyloxyphenethyl Alcohol was prepared in the same way as p-methoxyphenethyl alcohol. Reaction between 243 g of p-bromophenyl isopentyl ether, 24 g of magnesium, and 52 g of ethylene oxide gave 60.8 g (32%) of p-isopentyloxyphenethyl alcohol, b.p. 175-176° (15 mm) and m. p. 36-37°.

Its phenylurethan had m.p. 91-92° (from alcohol).

Found %: C 72.85; 72.81; H 7.59; 7.63; N 4.04; 4.17
$C_{20}H_{25}NO_3$. Calculated %: C 73.36; H 7.69; N 4.27

p-Isopentyloxystyrene was prepared in the same way as p-methoxystyrene by the dehydration of 52 g of p-isopentyloxyphenethyl alcohol with the aid of 18.2 g of potassium hydroxide in presence of 1 g of hydroquinone; the yield of p-isopentyloxystyrene, b. p. 161-163° (45 mm), was 13.7 g (29%).

SUMMARY

1. Five p-alkoxystyrenes were synthesized, and of these p-propoxy-, p-butoxy-, and p-isopentyloxy-styrenes were obtained for the first time.

2. It was shown that the glass transition temperatures of p-alkoxystyrenes fall with increase in the length of the radical of the alkoxy group and that the introduction of an oxygen atom between the alkyl radical and the aromatic nucleus in an alkylstyrene raises the glass point of the polymer obtained from it.

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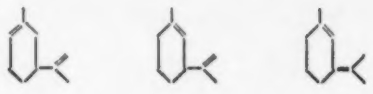
* In Russian.

BRIEF COMMUNICATIONS

RAMAN SPECTRA OF SOME TERPENES

M. I. Batuev, I. I. Bardyshev, and A. D. Matveeva

The terpenes investigated belong to the meta series:



sylvestrene isosylvestrene sylveterpinolene

They have the following physical constants:

Hydrocarbon	B.p. (°C at 20 mm)	n_D^{20}	d_4^{20}	MR	
				found	calculated
Sylvestrene	70	1.4740	0.8447	45.29	for
Isosylvestrene	64	1.4733	0.8381	45.62	$C_{10}H_{16}$ MR=45.26
Sylveterpinolene	74 (13 mm)	1.5076	0.8619	47.05	

The Raman spectra of these compounds were determined with a Soviet ISP-51 three-prism spectrograph having a central camera, and the exciting radiation was the 4358 A line of a mercury lamp. •

1. Sylvestrene Δν(см⁻¹): 168(1), 308(3), 335(3*), 365(2*), 425(4 db), 449(4), 468(1), 494(4), 545(1), 626(8), 649(0), 675(0), 690(3*), 714(3*), 757(1), 781(5), 805(3), 824(5), 848(0), 892(6 db), 920(1), 937(6), 993(4), 1014(5* b, db), 1037(1), 1062(4*), 1076(2*), 1111(4b, db), 1149(4), 1169(0), 1208(0), 1286(3), 1317(3*), 1337(3* db), 1397(2), 1434(9*), 1457(5*), 1646(7), 1677(7), 2834(4*), 2877(5*), 2911(10*), 2931(3*), 2964(3**) 2984(3**), 3039(2), 3080(3b).

2. Isosylvestrene Δν (см⁻¹): 155(4), 161(2), 183(1), 253(2), 312(2), 333(2), 368(1), 392(2), 421(2), 437(1), 470(1), 520(2), 545(2), 600(4), 611(6), 648(1), 701(4), 731(4), 772(5), 796(0); 840(5); 863(1), 887(6), 919(2), 947(6), 981(1), 1001(2), 1025(2), 1054(1), 1077(2), 1092 (4 b, db), 1159(2), 1188(2), 1222(2), 1261(2), 1290(2), 1313(1), 1397(2*), 1411(2), 1432(6*), 1450(3*), 1647(6), 1672(3), 2834(2*), 2856(4*), 2877(3*), 2911(4*), 2934(8*), 2984(4*), 3017(1), 3044(3), 3075(b).

3. Sylveterpinolene , Δν (см⁻¹): 169(1), 195(0), 280(1*), 300(0*), 342(2**), 357(2**), 378(5**), 423(3*), 438(3*), 475(2**), 494(2**), 518(1), 552(4), 601(6), 624(2), 747(5), 802(3), 837(3), 855(0), 877(5), 907(2), 969(7), 1009(3 db), 1043(3), 1067(5), 1112(7), 1148(2), 1178(8), 1204(7), 1257(3), 1283(9), 1225(bl), 1349(3h), 1375(8), 1430(6*), 1450(8* b), 1570(1), 1611(1), 1645(10* b), 1664(1*), 1714(1), 2725(2), 2829(4*), 2856(6*), 2870(6*), 2908(10*), 2926(6*), 2964(4*), 2991(2*), 3043(4), 3085(2).

• The symbols accompanying the intensities having the following meanings: b broad line; sh sharp line; db double line; the asterisks indicate lines on a background that is common to neighboring lines marked with the same number of asterisks.

The relative positions and character of the two double bonds in these compounds can be traced very clearly in these spectrum data.

In sylvestrene the two double bonds are remote from one another and it may be expected that they do not interact, i. e. are independent. In that case one of them can be regarded as the frequency of 1-methylcyclohexene and the other as the frequency of an asymmetrically disubstituted ethylene. In 1-methylcyclohexene the frequency of the double bond is raised to 1675 cm^{-1}, as compared with the frequency of the double bond in cyclohexene (1650 cm^{-1}). It is at this raised level that we find the frequency of the ring double bond in sylvestrene (1677 cm^{-1}). In ethylene the frequency of the double bond is 1621 cm^{-1}, and in asymmetrically dialkylethylenes it is raised to about 1650 cm^{-1}. In sylvestrene it is found at this raised value (1646 cm^{-1}). Hence, in sylvestrene the two double bonds, being fairly distantly removed from one another, do not in fact affect each other's vibrational frequencies (do not cause any marked shifts in these frequencies), i. e. are independent of one another.

In isosylvestrene the double bonds are closer together by one C–C linkage than in sylvestrene; in sylvestrene the ethylenic substituent is in the β-position with respect to the double bond of the ring, whereas in isosylvestrene it is in the α-position. There is a rule, however, concerning disubstituted cyclic hydrocarbons of this kind having one double bond in the ring: in β-substituted compounds the frequency of this bond is somewhat higher than in α-substituted compounds [1]. This rule was confirmed for the case of sylvestrene and isosylvestrene: the frequency is indeed somewhat higher (1675 cm^{-1}) for the first than for the second (1672 cm^{-1}). The frequency of the second double bond is 1647 cm^{-1}. The interval between the frequencies of the double bonds is somewhat narrower (25 cm^{-1}) than in sylvestrene (31 cm^{-1}), but it is nevertheless considerable; the intensities of these frequencies are comparatively low. All this indicates that there is no substantial interaction between the double bonds of isosylvestrene.

In sylveterpinolene the two double bonds are still closer together: they are already conjugated, and they interact strongly. The fact that one of the double bonds is outside the ring and the other is in the ring results in more complicated interaction (conjugation) than in, for example, 1,3-butadiene, 1,3-pentadiene, etc; whereas these last give one intense double-bond frequency (1638 and 1646 cm^{-1} respectively), the double bond region of the sylveterpinolene spectrum comprises not only the very intense frequency at 1645 cm^{-1}, but also four weak frequencies at 1570, 1611, 1664, and 1714 cm^{-1}.

SUMMARY

Investigation of Raman spectra indicates increase in the interaction between the double bonds as we pass from sylvestrene and isosylvestrene to sylveterpinolene and indicates that the character of the interaction in the last compound is more complex than in 1,3-butadiene and other similar conjugated systems.

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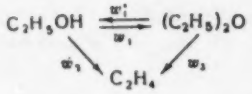
USE OF RADIOCARBON FOR THE INVESTIGATION OF THE MECHANISM OF THE DEHYDRATION OF ETHANOL OVER ALUMINA

A. A. Balandin, G. V. Isaguliants, E. I. Popov, Iu. I. Derbentsev and S. L. Vinogradov

The mechanism of the catalytic dehydration of ethanol has been discussed in the literature for many years. Some authors consider that the formation of ethylene passes through the stage of the formation of diethyl ether. Others consider that ethylene and ether are formed by two independent parallel reactions. Recently the question has been re-examined by Baleceanu and Jungers [1], Topchieva and Yung-P'ing [2, 3, 5], and Boreskov et al. [4].

The solution of the question of the actual mechanism of this complex reaction can be approached by determining the rates of the separate processes in Scheme (1):



(1)

In order to solve this question, in the present investigation we carried out the dehydration of ethanol to which C^{14}-labeled diethyl ether was added. As a result of reactions proceeding at the rates w_1, w_1', w_2, and w_3 [scheme (1)], the alcohol, ether, and ethylene will have specific radioactivities of α, β, and γ, respectively, and the rates w_1 and w_1' will be given by the equations (2):

$$w_1' = \frac{d\alpha}{d\tau}\,\frac{-c_1}{(\alpha-\beta)}\,; \qquad w_1 = \frac{d\beta}{d\tau}\cdot\frac{c_2}{(\alpha-\beta)}. \tag{2}$$

Here, c_1 and c_2 are the concentrations of alcohol and ether, and τ is the time of contact. We further have

$$dI_3/d\tau = w_2\alpha + w_3\beta;\ I_3 = \gamma c_3; \qquad dc_3/d\tau = w_2 + w_3, \tag{3}$$

in which I_3 is the total activity and c_3 the concentration of ethylene; hence $w_2\alpha + w_3\beta = c_3 \cdot d\gamma/d\tau + \gamma dc_3/d\tau$ from which it is easy to show that

$$w_3 = \frac{c_3 \cdot d\gamma/d\tau + (\gamma-\alpha)\,dc_3/d\tau}{\beta-\alpha} \tag{4}$$

On the basis of our experimental data, in the present investigation we have determined the rates of all the process in Scheme (1) with the aid of Equations (2)–(4).

We investigated the dehydration of ethanol in a flow apparatus [7] with 2.8 g of catalyst (A-2 active alumina having 0.5-mm to 1-mm granules). The reaction products were collected in a receiver cooled to −50°.

Ethylene was collected in a gas holder over brine. The activity of the catalyst was constant, and highly reproducible results were obtained.

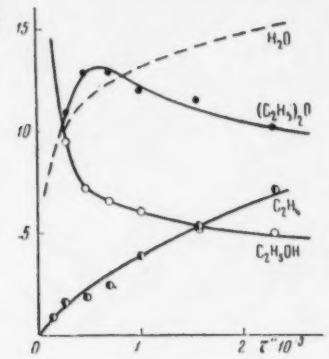


Fig. 1

C^{14}-labeled ether was synthesized from labeled ethanol in presence of a catalyst prepared from potash alum [8]. Radioactivity was measured as in previous investigations [6]. Two series of experiments were carried out. We first carried out a preliminary series without labeled substances in which we determined the variation in the concentrations of alcohol, ether, ethylene, and water with the time of contact. We then carried out experiments with additions of labeled ether (3.8%); in these we determined the variation in the specific activities of alcohol, ether, and ethylene with time of contact. Rectified alcohol of d_4^{20} 0.8070 was used in the experiments.

For the determination of ethanol and ether in the catalyzate we used a method on the oxidation of alcohol and ether with dichromate in sulfuric acid. For radiochemical analysis the condensate was fractionated through a column. An ether fraction (33.4-34°) and an alcohol fraction (76.5-78°) were collected. Special experiments on the separation of highly active alcohol and inactive ether, and of highly active ether and inactive alcohol showed that the isolation of pure alcohol and ether was attained in this column.

Figure 1 represents experiments on the dehydration of alcohol at 300° (without addition of labeled ether). The abscissae are times of contact, which are expressed by $\tau = d \cdot 3600/n \cdot 46$, in which d is the bulk density of the catalyst, n is the number of moles of alcohol passed per ml of catalyst per hour. The ordinates are concentrations of alcohol, ethylene, and water, expressed as millimoles per gram of original alcohol. For ether these values are doubled.

Reaction rate ($\times 10^3$ m mol./g per sec)	τ ($\times 10^3$ seconds)							
	0.2	0.4	0.6	0.8	1.0	1.4	1.8	2.2
w_1	34	20	12	7.1	5.1	3.7	3.2	3.0
w_1'	5.4	8.3	8.8	6.7	4.4	3.0	2.7	2.4
w_2	3.3	1.9	1.35	1.2	1.0	0.9	0.8	0.7
w_3	1.1	1.8	1.85	1.5	1.3	1.1	0.9	0.8

Figure 2 represents experiments on the dehydration of ethanol with an addition of labeled ether. The abscissae are times of contact, and the ordinates are specific activities (% on the original activity of the ether). From the data of Figures 1 and 2 and Equations (2)—(4), the reaction rates in Scheme (1) were calculated. The results of the calculations are given in the table.

The maximum rates of conversion of ether into alcohol, $W_1' = 8.8$ at $\tau = 0.6 \cdot 10^3$ seconds, and of ether into ethylene, $w_3 = 1.85$ at $\tau = 0.6 \cdot 10^3$ seconds (see table), are in close accord with the maximum concentration of ether at τ = about $0.6 \cdot 10^3$ seconds (Fig. 1). The rates of conversion of ether and of alcohol into ethylene are very close and can be distinguished only in the region in which the difference in the concentrations of alcohol and ether is fairly great. It is interesting that the rates w_1 and w_1' vary in a similar way, though in absolute value these rates are considerably greater than the rates w_2 and w_3. From this we may draw the important conclusion that ethylene is formed from alcohol and ether at almost equal rates and equilibrium is rapidly established between alcohol and ether.

This relation of rates satisfactorily explains the presence of maxima in ether concentration, when expressed as a function of time of contact in the dehydration of ethanol, and in the concentration of ethanol in the dehydration

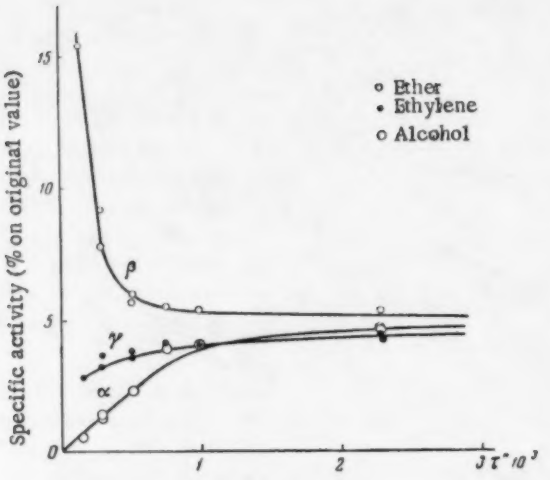


Fig. 2

of ether; the relation does not correspond to a scheme of consecutive reactions. It follows from our results that decomposition of ether into molecules of alcohol and ethylene is not the main path in the conversion of ether into alcohol, since in that case the rate w_1' should be less than or equal to the rate w_3.

SUMMARY

1. The rates of the dehydration of ethanol and of ether into ethylene and of the interconversion of alcohol and ether were determined for reaction over alumina at 300°.

2. The results show that ethylene is formed by two routes: directly from alcohol, and via ether.

3. The relative rates found satisfactorily explain the character of the kinetic curves.

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MODIFICATION OF THE PROTEIN MOLECULE

COMMUNICATION 2. ATTACHMENT OF AMINO ACIDS AND PEPTIDES AT CARBOXY GROUPS OF THE PROTEIN MOLECULE

K. T. Poroshin

Among the numerous methods for the chemical modification of proteins, the most interesting are those in which addition of amino acids is effected through the peptide link. A protein can be regarded as a polyelectrolyte and multifunctional system in which amino and carboxy groups can take part in the formation of peptide links. The attachment of amino acids to protamines [1], gelatin [2], albumin [3], and the hydrolyzate of casein peptone [4] was effected through the amino groups of these proteins. These chemical modifications of the protein molecule resulted in the appearance of new physical, physicochemical, and biological properties.

In our investigation we undertook the task of introducing amino acids and peptides into the protein molecule by attachment at carboxy groups. As proteins we selected casein and egg albumin. We used casein because it can be regarded as a weak polybasic acid in which the free carboxy groups belong to nonamidated residues of aspartic and glutaric acids and to terminal residues. In casein there are about 150 moles of glutaric acid residues and about 50 aspartic acid residues per 10^5 g. The benzyloxycarbonyl derivative of casein was used for reaction. We used also egg albumin, in which terminal amino groups are absent and there are about 50 carboxy groups per molecule (for a molecular weight of 45,000).

By treatment with ethyl chloroformate the carboxy groups of proteins were converted into mixed anhydrides, and these were used in reactions with the hydrochlorides of suitable amino esters and peptides. The chemical modification of the protein molecule can be represented as follows:

$$m\ C_6H_5CH_2OCOCl + (NH_2)_m\text{-protein mol.}\text{-}(COOH)_n \xrightarrow[pH\ 8.5]{0^\circ} (CbZONH)_m\ \text{protein mol.}\text{-}(COOH)_n \quad (I)$$

$$(I) + ClOCOH_5C_2 \xrightarrow[pH\ 7.5,\ (C_2H_5)_3N]{0^\circ} (CbZONH)_m\text{-protein mol.}\text{-}\left(C(=O)\text{-}O\text{-}C(=O)\text{-}OH_5C_2\right)_n \quad (II)$$

$$(II) + HCl\ NH_2CHR\,COOR' \xrightarrow[pH\ 7.5,\ (C_2H_5)_3N]{0^\circ} (CbZONH)_m\text{-protein mol.}\ (CONHCHRCOOR')_n \quad (III)$$

$$III) \xrightarrow{NaOH} CbZONH)_m\text{-protein mol.}\cdot(CONHCHR\,COOH)_n \quad (IV)$$

$$(IV) \xrightarrow[H]{Pd} (NH_2)_m\text{-protein mol.}\ (CONHCHR\,COOH)_n \quad (V)$$

CbZO=$C_6H_5CH_2OCO$-; R=H &CH_3; R'=CH_3-&C_2H_5-.

EXPERIMENTAL

The casein preparations were obtained in the form of Perov's caseinic acid [5]. This protein had the following characteristics: titration value (volume (ml) of 0.1 N NaOH required for the neutralization of 1 g of protein in presence of phenolphthalein as indicator) 8.35, total nitrogen 15.60%, amino nitrogen 0.32. The other protein preparation was water-soluble egg albumin which contained no amino nitrogen determinable by the van Slyke method.

Preparation of Benzyloxycarbonylcasein (I). Benzyl chloroformate was added dropwise at 0° to a sample of the protein dissolved in sodium hydroxide solution or a pH 8.5 phosphate buffer with constant stirring. After reaction for 30 minutes the solution was treated twice with ether. The aqueous layer was acidified to Congo red with 10 N HCl. The precipitate was washed with distilled water, with alcohol, and finally with dry ether. The preparation was dried for 2-3 days over sulfuric acid in a desiccator and then investigated. The benzyloxycarbonylcasein did not contain amino nitrogen.

Reaction of Benzyloxycarbonylcasein with Ethyl Chloroacetate (II)*. Triethylamine (1-1.5 ml) was added to a sample of benzyloxycarbonylcasein (usually 0.2-0.3 g) suspended in 6-10 ml of dry chloroform. The protein preparation dissolved and a solution of pH 7.5-7.8 was formed. The solution was cooled to 0°, and 1-1.5 ml of ethyl chloroacetate was added gradually, when the pH fell to 4.2-4.5.

Condensation of the Mixed Anhydride of Benzyloxycarbonylcasein with Ethyl Esters of Amino Acids (III). A mixture of the hydrochloride of the ethyl ester of the amino acid (glycine or DL-alanine) and triethanolamine in chloroform was cooled to 0° and added slowly to the compound (II) within 15 min after its preparation. The reaction mixture was left at room temperature for 30 minutes. The compound formed (III) was washed successively with 10 ml of distilled water, 1 N HCl, and 5 ml of 0.5 N $NaHCO_3$. During washing a clot of protein formed at the chloroform-water interface and was transferred to a thimble for dialysis against distilled water in order to remove mineral compounds and unchanged amino acid. The dialyzate and wash liquors were investigated chromatographically. It was shown that about 20% of the amino ester hydrochloride on the weight of protein reacted with the latter. After dialysis the protein derivative was washed with water, dehydrated with alcohol, treated with dry ether, and dried over sulfuric acid in a desiccator. The preparation did not contain amino nitrogen. The ethoxycarbonyl content, determined according to Viebock and Brecher, was 5.9%.

Condensation of the Mixed Anhydride of Benzyloxycarbonylcasein with Peptide Esters (III). A mixture of the hydrochloride of diglycine ethyl ester or the hydrochloride of DL-alanyldiglycine and the calculated amount of triethylamine in chloroform was cooled to 0° and added slowly to the compound (II) within 15 min after its preparation. The further operations were carried out as in the experiments with amino esters. For the determination of the amount of peptide that reacted we used the method developed by us [6]. For reaction at the carboxy groups of 200.4 mg of benzyloxycarbonylcasein, 85.4 mg of the hydrochloride of alanyldiglycine methyl ester was required. A 199.2-mg sample of the same casein derivative required 65.3 mg of the hydrochloride of diglycine ethyl ester. Amino nitrogen was absent in the compound obtained (III). The preparations were precipitated at pH 4.7 and had the same titration values as the original samples.

Hydrolysis of the Ester Groups of the Protein (IV). A 222.7-mg sample of (III) was added to 10 ml of acetone, and 10 ml of 1 N NaOH was added, when the precipitate dissolved. After 90 minutes the solution was acidified with HCl to pH 4.5. The precipitated protein was dialyzed off in the course of two days and was then dehydrated with alcohol, treated with ether, and dried in a desiccator over sulfuric acid. The preparation contained no free amino nitrogen and did not contain ester groups.

Removal of Benzyloxycarbonyl Groups (V). This operation was carried out by catalytic reduction over palladium black [7]. The yield of benzyloxycarbonyl-free product was 70%. The preparation contained 0.35-0.40% of amino nitrogen and did not contain ester groups determinable by Viebock and Brecher's method.

Egg Albumin was also used as a protein preparation for experiments on the attachment of amino esters and peptide esters. The experiments were carried out similarly. Up to 6.8% of amino ester hydrochloride and up to 4.0% of peptide ester reacted with the protein preparation.

* In the introduction and reaction scheme it is indicated that ethyl chloroformate, not chloroacetate, was used. – Publisher.

SUMMARY

By the attachment of the ethyl esters of glycine, DL-alanine, and diglycine and of the methyl ester of DL-alaninediglycine at the carboxy groups of casein and egg albumin, derivatives of these proteins were prepared.

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**In Russian.

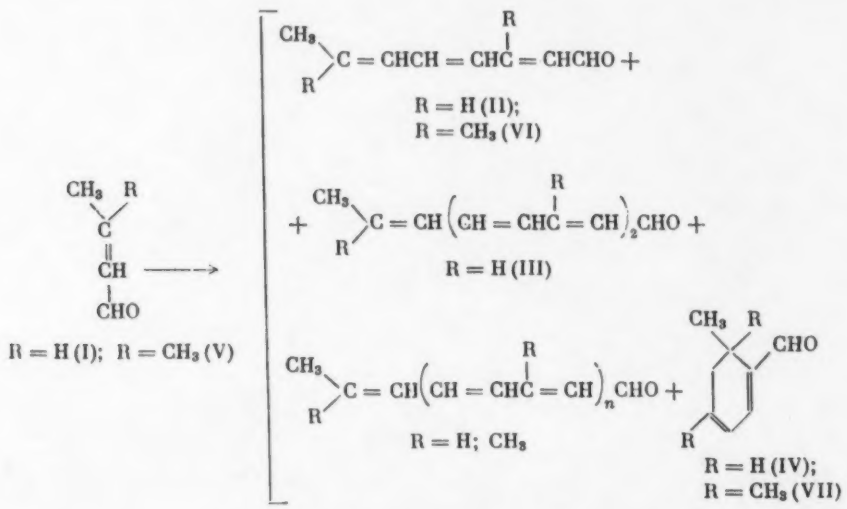
POLYENE CONDENSATION OF ALDEHYDES

I. N. Nazarov and Zh. A. Krasnaia

The preparation of polyenic aldehydes by the crotonic condensation of acetaldehyde, crotonaldehyde, and other aldehydes has long attracted the attention of investigators. If the method of polyenic condensation of aldehydes is adequately developed it will undoubtedly provide the simplest means of synthesizing polyenals.

In connection with our recent investigations on the synthesis of polyenic isoprenoid compounds, we decided to make a detailed systematic study of the polyenic condensation of aldehydes as affected by reaction conditions: catalyst, temperature, and time. It would be highly desirable to learn how to control this reaction so as to obtain any one product predominantly, for in the polyenic condensation of aldehydes in presence of secondary amines under acid conditions (as pointed out earlier by Kuhn [1] and Fischer [2]) a whole range of different aldehydes having open-chain and cyclic structures is formed. The resulting complex mixture is not easily resolved, particularly as we are dealing with polyenals that are extremely sensitive to atmospheric oxygen; moreover, the polyene condensation is generally accompanied by considerable resinification.

As object for investigation we selected, in the first place, the readily available crotonaldehyde (I).



As catalysts we used mixtures of acetic acid and various amines. As would be expected, tertiary amines did not bring about condensation; neither did aromatic and aliphatic-aromatic amines (diphenylamine and N-methylaniline) have any condensing effect on crotonaldehyde. Secondary aliphatic amines (dimethylamine, diethylamine, dibutylamine, diisobutylamine) brought about condensation, and as in the case of piperidine we obtained a mixture of substances consisting of 2,4,6-octatrienal (II), higher polyenals, 6-methyl-1,3-cyclohexadiene-1-carboxaldehyde (IV), resin, and unchanged crotonaldehyde.

The results with secondary aliphatic amines as catalysts are peculiar in that a considerable amount of 6-methyl-1,3-cyclohexadiene-1-carboxaldehyde (IV) is formed (30-36%), and the fraction corresponding in boiling point to higher polyenals contains much noncrystallizing material, which probably consists of cyclic aldehydes. 2,5-Dimethylpiperidine and decahydro-2-methylquinoline had almost the same effect as piperidine itself. We usually used about 3% of piperidine on the weight of crotonaldehyde; use of 10% led to reduction in the yield of polyenals and increase in the amount of resin. It is known from the literature [3] that addition of benzylamine to piperidine greatly increases its activity as catalyst in Knoevenagel reactions, e.g. in the reaction of cyanoacetic ester with ketones. However, addition of benzylamine to piperidine did not affect the yield of polyenals obtained from crotonaldehyde.

We investigated also the condensation of crotonaldehyde in presence of a mixture of piperidine and orthophosphoric acid. It was found that in presence of this catalyst 6-methyl-1,3-cyclohexadiene-1-carboxaldehyde (IV) was completely absent from the reaction products. 2,4,6-Octatrienal (II) and higher polyenals were here formed in approximately the same yield (22% and 21%) as in the best experiment with piperidine acetate.

In attempts to effect the synthesis of polyenals in presence of sodium ethoxide, even under strong cooling (– 70°) the whole of the crotonaldehyde was converted into a nondistilling highly visoous product containing hydroxy groups. We did not succeed in dehydrating it and in isolating any pure substances. It appeared that far-reaching aldol condensation of the crotonaldehyde occurred.

We studied the effect of temperature and duration of reaction on the yield of polyenals for the case of the condensation of crotonaldehyde in presence of piperidine acetate. The best result was obtained by heating the reaction mixture for 90 minutes at 100°. We then obtained 22% of crystalline 2,4,6-octatrienal (II) and 19% of a mixture of higher polyenals, from which we isolated 2,4,6,8,10-dodecapentaenal (III).

From an examination of the reaction of polyene condensation it would appear that water should hinder the reaction, but we did not observe this. When 17% of water was added to crotonaldehyde, the result of the reaction was almost unchanged. When the condensation was carried out in benzene, the yield of polyenals was somewhat lower than in absence of solvent. Azeotropic removal of water formed in the reaction did not result in increased yield of polyenals, neither did the addition of freshly dehydrated silica gel to the crotonaldehyde.

We studied also the polyene condensation of senecialdehyde (V), and this was found to be the same in character as that of crotonaldehyde (I). From the products of the reaction of senecialdehyde we isolated "dehydrocitral" (3,7-dimethyl-2,4,6-octatrienal) (VI), m. p. 40-41°, in 14.5% yield; the yield of higher polyenals was about 15%.

EXPERIMENTAL

Synthesis of Polyenals from Crotonaldehyde (I). A mixture of 0.5 ml of piperidine and 0.5 ml of glacial acetic acid was added with stirring to 35 g of freshly distilled crotonaldehyde (I). The bright-red reaction mixture was heated for 45 minutes in a boiling water bath; a second portion of catalyst (0.5 ml of piperidine and 0.5 ml of acetic acid) was then added, and heating was continued for 45 minutes further. Distillation of the reaction mixture at a residual pressure of 18 mm resulted in the collection of 5 g of crotonaldehyde and 1.6 ml of water in a cooled trap. The residue was diluted with ether, filtered, washed with water, and dried with calcined magnesium sulfate. Distillation gave the following fractions:

Fraction I,	b.p. 70—72°	(10 mm); 2.3 g	n_D^{20} 1.4908
Fraction II,	b.p. 52—60°	(0.2 mm); 6.7 g	
Fraction III,	b.p. 110—140°	(0.2 mm); 5.5 g	
Resinous residue		6.4 g	

Fraction I was 6-methyl-1,3-cyclohexadiene-1-carboxaldehyde (IV); the semicarbazone of (IV) had m.p. 199-200°, which is in accord with the literature [4]. Fraction II was 2,4,6-octatrienal (II) (22% yield), m. p. 57-58° after two crystallizations from petroleum ether, which coincides with data in the literature [5].

The 2,4-dinitrophenylhydrazone of (II) melted with decomposition at 189°; λ_{max} (in isooctane) 372, 390, and 406 mμ.

Found %: N 18.34; 18.28
$C_{14}H_{14}N_4O_4$. Calculated %: N 18.55

From Fraction III we isolated 2,4,6,8,10-dodecapentaenal (III) in the form of golden-yellow needles, m.p. 159-161° (from glacial acetic acid), which corresponds to data in the literature [2].

Found %: C 82.76; 83.27; H 8.30; 7.80
$C_{12}H_{14}O$, Calculated %: C 82.71; H 8.10

SUMMARY

The effects of catalyst, temperature, and duration of reaction were studied for the polyenic condensation of crotonaldehyde and senecialdehyde.

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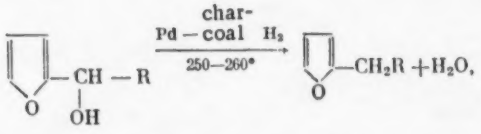
CATALYTIC REDUCTION OF α-ALKYLFURFURYL ALCOHOLS TO ALKYLFURANS

N. I. Shuikin and I. F. Bel'skii

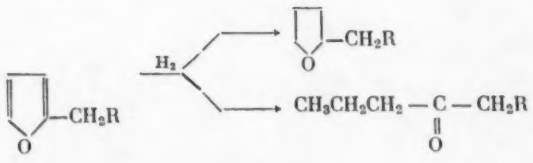
In the investigation of the vapor-phase hydrogenation of α-methyl- and α-ethylfurfuryl alcohols over palladized charcoal at 200-230° [1] we came across the interesting fact of the selective reduction of these compounds into 2-ethyl- and 2-propyl-furans respectively. We showed that ability of the hydroxy group to be replaced by hydrogen under the catalytic action of palladized charcoal depends on the presence of the furan ring in the molecule of the alcohol; with the hydrogenation of the nucleus into a tetrahydrofuran ring the tendency of the hydroxy group to be replaced by hydrogen disappears. Similarly, the bond between carbon and hydroxyl in a secondary aliphatic alcohol (2-pentanol) was found to be quite stable under the conditions of reduction over palladized charcoal. The direct catalytic reduction of α-alkylfurfuryl alcohols into alkylfurans is of obvious practical importance in that it makes it possible to replace the stages of dehydration of α-alkylfurfuryl alcohols and hydrogenation of alkenylfurans by the single stage of reduction of α-alkylfurfuryl alcohols.

In present work we investigated the vapor-phase hydrogenation of α-isopropyl- and α-butyl-furfuryl alcohols over palladized charcoal at 250-260°. In accord with our previous observations we found that under these conditions hydroxyl is replaced by hydrogen with the result that α-isopropyl- and α-butyl-furfuryl alcohols are converted into 2-isobutyl- and 2-pentyl-furans, respectively, in 65-70% yield:



$R = i\text{-}C_3H_7$ or $n\text{-}C_4H_9$.

In addition to these main products the catalyzates contained small amounts of 2-isobutyl- and 2-pentyl-tetrahydrofurans and also 2-methyl-4-heptanone and 4-nonanone. These compounds are formed as secondary products of the hydrogenation and hydrogenolysis of the alkylfurans [2]:



EXPERIMENTAL

α-Isopropyl- and α-butyl-furfuryl alcohols were prepared by the Grignard reaction from 2-furaldehyde and the corresponding alkyl bromides in about 60% yield.

α-Isopropylfurfuryl alcohol had the followin properties: b. p. 66-68° (3 mm); d_4^{20} 1.0312; n_D^{20} 1.4783. α-Butylfurfuryl alcohol had b.p. 85-87° (3 mm); d_4^{20} 1.0030 and n_D^{20} 1.4765. The preparation of the catalyst (palladized charcoal) is described in [1].

The alcohols were passed in 100-g portions over the catalyst at a space velocity of 0.1 $hour^{-1}$. The catalyzates were fractionated through a column having an efficiency of 40 theoretical plates. The alkylfurans isolated had the following properties: 2-isobutylfuran, b. p. 128-129° (750 mm), d_4^{20} 0.8785; n_D^{20} 1.4415; 2-pentylfuran, b.p. 163.6-164° (745 mm); d_4^{20} 0.8835; n_D^{20} 1.4512.

SUMMARY

In the vapor-phase reduction of α-isopropyl- and α-butyl-furfuryl alcohols over palladized charcoal at 250-260°, 2-isobutyl- and 2-pentyl-furans are formed in yields of up to 70%.

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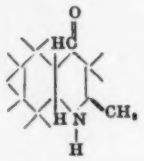
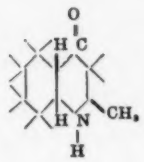
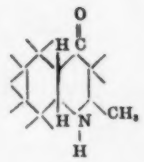
DIPOLE MOMENTS OF STEREOISOMERS OF OCTAHYDRO-2-METHYL-4(1H)-QUINOLONE

A. N. Shidlovskaia, Ia. K. Syrkin, I. N. Nazarov, and D. V. Sokolov

The dipole moments of three stereoisomers of octahydro-2-methyl-4(1H)-quinolone synthesized by Sokolov were measured. Dielectric polarizations were determined by the heterodyne method in benzene solutions at 25°. The results are given in the table, which shows the formulas, melting points, range of concentrations investigated, total polarizations P_{∞}, orientation polarizations P_{or}, and the dipole moments. The electron polarization was calculated from the refractions of the bonds; it was 47.8 cc. In the calculation of dipole moments, the Hedestrand equation was used.

No.	Formula of compound	M.p. (°C)	Concentration (mole fraction)	P_{∞}	P_{or}	$\mu \cdot 10^{18}$
1		38—39	0.00259—0.00270	189.85	142.02	2.61
2		62—63	0.00217—0.00785	193.30	145.47	2.64
3		41—42	0.00224—0.00436	192.12	144.29	2.63

Within the limits of experimental error the moments of the three isomers are the same. Since in these compounds the dipole moment is determined by the positions of the vectors of the C=O, N—H, and C—H moments, we may conclude from these results that these groups are directed similarly in the three isomers.

SUMMARY

The dipole moments of three isomeric octahydro-2-methyl-4(1H)-quinolones were measured. The identity of the moments for all the isomers indicates that the polar groups have the same configuration in the three isomers.

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REACTION OF FERROCENE WITH OLEFINS

A. N. Nesmeianov and N. S. Kochetkova

In three previous communications we reported work on the alkylation of ferrocene with alkyl halides by the Friedel-Crafts reaction [1-3]. In the last of these we described also the alkylation of ferrocene with isobutene in presence of aluminum chloride. We now make a preliminary report on the alkylation of ferrocene with ethylene and propene and its polyalkylation with isobutene. The reaction was carried out at 100-150° in a rotating autoclave in presence of aluminum chloride (10-20%) (solvent heptane).

Thus, by the action of ethylene under pressure (30-40 atm) we obtained a mixture of ethylferrocene [20.5%; b.p. 106° (4 mm)], diethylferrocene [5.5%; b.p. 125-126° (4 mm)], and polyethylferrocenes [4.5%; b.p. 150-180° (4 mm)]. By the action of propene under pressure (5-10 atm) we obtained a mixture of isopropylferrocene (30%), b.p. 106-107° (3 mm), diisopropylferrocene (13.8%), b.p. 135-136° (3 mm), and polyisopropylferrocenes (13.3%), b.p. 150-160° (3 mm). By the action of isobutene at 100°, in addition to mono- and di-tert-butylferrocenes obtained previously [3], we obtained tri-tert-butylferrocene (43.5%), m.p. 88°, and tetra-tert-butylferrocene (21.4%), b. p. 195-200° (3 mm).

Infrared-spectrum measurements on tri- and tetra-tert-butylferrocenes showed the absence of characteristic frequencies at 1000 and 1107 cm^{-1} (free cyclopentadiene ring or ferrocene), so that the alkyl groups of these substances are present in both cyclopentadiene nuclei. On the other hand the infrared spectrum of pentamethylferrocene, obtained by the methylation of ferrocene with methyl bromide at 50-60° in presence of aluminum chloride in an autoclave, contains characteristic frequencies at 1003 and 1107 cm^{-1}, so that all five methyl groups must be in the same cyclopentadiene nucleus.

SUMMARY

1. The alkylation of ferrocene with ethylene and propene and its polyalkylation with isobutene were carried out in presence of anhydrous aluminum chloride.

2. Mixtures of the corresponding ferrocene homologs were obtained in yields of 35-70%.

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*Original Russian pagination. See C. B. Translation.

SYNTHESIS OF ETHYLENE COPOLYMERS

G. S. Kolesnikov and T. A. Soboleva

We have shown [1] that ethylene polymerizes under a pressure of 50 atm in presence of tributylborine; somewhat earlier one of us in collaboration with Fedorova [2] and Klimentova [3] found that tributylborine is a catalyst for the polymerization of acrylonitrile, styrene, and methyl methacrylate. In view of these observations we considered it to be of interest to determine the possibility of synthesizing copolymers of ethylene with these unsaturated compounds in presence of tributylborine as polymerization catalyst.

EXPERIMENTAL

With this object we carried out several experiments by the following procedure. A mixture of 100 ml of dry toluene, 1.72 g of tributylborine, and 0.164 mole of liquid monomer was prepared in a 500-ml stainless steel rotating autoclave, and ethylene was passed in from a compressor until the pressure attained 100 atm. The autoclave was rotated for three hours at room temperature; the pressure fell to 40-50 atm in the first 10-15 minutes. The temperature was then raised to 50° and was maintained at this level for two hours with continuous rotation; heating was stopped, and the autoclave was left stationary overnight. The reaction mixture was diluted with 150-250 ml of methanol and washed out with water; organic solvents and unchanged monomer were steam-distilled off, and the copolymer obtained was dried to constant weight at 50°. The dry copolymer was dissolved in dichloroethane (2.5% solution), and the copolymer was reprecipitated by adding this solution dropwise into ten times its volume of methanol with vigorous stirring; in the case of the ethylene-acrylonitrile copolymer the solvent used was dimethylformamide. The reprecipitated copolymer was washed with methanol and dried to constant weight at 50°. The composition of the copolymer was calculated from the results of elementary analysis. The results are given in the table.

Ethylene Copolymers

Monomer	Copolymer obtained (g)	Elementary composition (%)			Content in copolymer (moles %)	
		C	H	N	ethylene	monomer
Methyl methacrylate	5.5	64.25 64.23	8.75 8.79		41.5	58.5
Styrene	1.2	91.62 91.18	8.11 8.50		29.0	71.0
Acrylonitrile	5.0			20.53 20.43	35.0	65.0
Vinyl acetate	2.0	80.24 80.21	10.68 10.77		93.2	6.8

The complete solubility in dichloroethane of the products of the copolymerization of ethylene with methyl methacrylate, styrene, and vinyl acetate indicates that these products are copolymers or mixtures of copolymers with polymers of the liquid monomers and are not mixtures of polyethylene with the various homopolymers; otherwise part of the reaction product (polyethylene) would not dissolve in dichloroethane. As polyethylene is

insoluble in dimethylformamide, the complete solubility of the product formed in the copolymerization of ethylene with acrylonitrile in this solvent indicates that in this case also a copolymer is formed.

SUMMARY

Copolymers of ethylene with styrene, methyl methacrylate, acrylonitrile, and vinyl acetate were prepared by reaction in toluene in presence of tributylborine as polymerization catalyst.

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CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE WITH OLEFINS

COMMUNICATION 19. HYDROCONDENSATION OF CARBON MONOXIDE WITH 2-PENTENE. INTERCONVERSION OF 2- AND 1-PENTENES UNDER THE CONDITIONS OF THIS REACTION

Ia. T. Eidus and M. B. Ordian

We have previously [1] reported results of an investigation of the behavior of 1-pentene under the conditions of the catalytic hydrocondensation of carbon monoxide with olefins [2]. In the present paper we report the corresponding results for 2-pentene.

2-Pentene was synthesized from C_2H_5Br and $HCOOCH_3$, through the stage of 3-pentanol [3] and its acetic ester, with pyrolysis of the latter [4]; it had b.p. 36.3° (760); d_4^{20} 0.6500; n_D^{20} 1.3805. The catalyst, apparatus, and experimental procedure were the same as in previous investigations [1, 2]. The catalyzates were fractionated through a column of copper spirals having an efficiency of 40 theoretical plates. All experiments were carried out at atmospheric pressure at 190°. The other experimental conditions and the results are given in Table 1.

In absence of H_2 and CO 2-pentene did not suffer any change over the catalyst (Table 1, Experiment 343). In experiments with 2-pentene in a stream of H_2 (Table 1, Experiment 344) the original vapor-gas mixture had the composition C_5H_{10} 55.4%, H_2 44.6%. We collected 1.6 liters (STP) of gas of composition C_nH_{2n} 5.2%, H_2 73.1%, and C_nH_{2n+2} 21.7%. The amount of hydrogen entering the reaction was 7.8 liters (STP). When the liquid catalyzate was heated to 22° 450 ml of gas was liberated; its composition (determined by the chromathermographic method on silica gel [5]) was C_2H_6 9.0%, C_2H_4 26.0%, C_3H_8 28.2%, and C_4H_{10} 36.8%. After being freed from gas, the catalyzate (42.5 ml) was fractionated through a column. Table 2 gives the yields and constants of the fractions obtained. Fractions I and II (Table 2) were investigated by the Raman spectrum method.* It was shown that Fraction I contained n-pentane (401, 840 cm^{-1}), 1-pentene (385, 435, 852, 1292, 1302, 1642 cm^{-1}), cis-2-pentene (1660 cm^{-1}), and trans-2-pentene (409, 484, 1674 cm^{-1}), the proportions of these three olefins being 1:1:2. Fraction II contained n-pentane (401, 840 cm^{-1}), cis-2-pentene (859, 1660 cm^{-1}), and trans-2-pentene (409, 484, 1674 cm^{-1}), the relative amounts of the last two being 3:7.

From these data and also from Table 2 it follows that in presence of hydrogen 2-pentene is hydrogenated to pentane to the extent of about 50%, isomerized to 1-pentene to the extent of 1.5-2.0%, converted into higher hydrocarbons to the extent of 6.5%, and, as shown by the amount and composition of the gas liberated, subjected to hydrocracking to the extent of about 4%.

2-Pentene in a Stream of $CO-H_2$ Mixture. In the experiments with 2-pentene in a $CO-H_2$ mixture (Table 1, Experiments 345, 346) the original vapor-gas mixture had the composition: C_5H_{10} 60-62%, H_2 32-33%, and CO 5.8-6.3%. In Experiments 345 and 346 we collected 13.8 and 4.9 liters (STP) of gas of composition: CO_2 0.7 and 0.5%, C_nH_{2n} 1.7 and 2.9%, CO 10.8 and 11.2%, C_nH_{2n+2} 9.9 and 17.2%, respectively. From the catalyzates, heated to 22°, we obtained 1135 and 560 ml (STP) of gas respectively. A mixture of the two portions of gas had the composition (determined by the chromathermographic method): C_2H_6 9.6% C_3H_8 24.8%, C_4H_8 38.7%, and C_4H_{10} 26.9%. The amounts entering into reaction (liters at STP) were H_2 20.8 and CO 4.2 in Experiment 345 and H_2 9.5 and CO 1.9 in Experiment 346. When the liquid catalyzates had been freed from gases (Experiments 345 and 346), the part boiling below 40° (corresponding to pentenes and pentane) was distilled off. Like fractions

*The spectra were determined and studied in the laboratory of the Commission on Spectroscopy of the Academy of Sciences of the USSR by V. T. Aleksanian and Kh. E. Sterin, to whom the authors express their thanks.

TABLE 1

Experiment No.	Catalyst No.	Duration of experiment (hr)	Amount passed			Space velocity ($hr.^{-1}$)			Amount of liquid catalyzate		Gas contraction (%)	Properties of liquid hydrocondensate after removal of gas			
			2-pentene (ml)	H_2 (liters at STP)	CO (liters at STP)	2-pentene	Outgoing gas	Whole vapor-gas phase	(ml)	(%/vol. of original 2-pentene)		d_4^{20}	n_D^{20}	Bromine value	Content of unsaturated hydrocarbons (%)
343	95	5	30'	—	—	0.20	—	41	28.2	94,0	—	0.6500	1.3805	229	100
344	95	9	50	9.0	—	0.18	33	74	45.6	91.2	82.2	0.6359	1.3669	83.4	37
345	96	49	285.5	31.4	5.7	0.19	25	66	246,0	86.1	63.5	0.6547	1.3802	50.6	42
346	96	18.5	102.0	12,8	2.4	0.18	27	68	93.0	91.1	67.8	—	—	—	—

TABLE 2

Fraction No.	B.p. (°C at 760 mm)	Yield (% by vol.)	n_D^{20}	d_4^{20}	Bromine value	Content of unsaturated hydrocarbons (%)
I	32.4—35.8	16.4	1.3648	0.6322	95.0	42.1
II	36.1—36.3*	70.0	1.3652	0.6335	87.6	38.8
Residue	(50—178)**	6.8	1.3898	0.6830	45.7	27.9
Losses	—	6.8	—	—	—	—

* Less than 0.5% of the 35.8-36.1° fraction was obtained.

** The residue was distilled from a Wurtz flask.

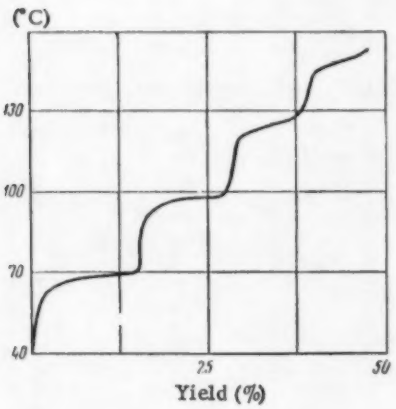
TABLE 3

Fraction No.	B.p. (°C at 760 mm)	Yield (% by vol.)	n_D^{20}	d_4^{20}	Bromine value	Content of unsaturated hydrocarbons (%)
I	30.9—35.8	8.8	1.3711	0.6396	141.7	62.3
II	35.8—37.1	67.3	1.3745	0.6445	175.9	78.0
Residue	—	13.5	1.4080	0.7166	59.1	50.3
Losses	—	10.4	—	—	—	—

TABLE 4

Fraction No.	B.p. (°C at 760 mm)	Yield (% by vol.)	n_D^{20}	d_4^{20}	C_n
I	44—58*	0.9	1.3614	—	—
II	60—71	16.3	1.3738	0.6569	C_6
III	79—87	0.9	1.3786	—	—
IV	87—94	2.6	1.3834	—	C_6+C_7
V	94—100	11.1	1.3873	0.6835	C_7
VI	106—131	11.1	1.3963	0.7010	C_8
VII	131—141	1.3	1.4010	—	—
VIII	141—151	8.6	1.4052	0.7175	(C_9)
Residue	(171—200)	39.5	—	—	—

* Fractions obtained in less than 0.5% yield are not given.



from the two catalyzates were combined, and their constants were determined. The results are given in Table 3. In all, 274 ml of catalyzate was taken for fractionation. As can be seen from Table 3 and as the investigation of Raman spectra shows, Fraction I consisted of cis- and trans-2-pentenes, pentane, and 1-pentene, and Fraction II consisted of the two forms of 2-pentene and pentane, the content of the latter being about 20-25%. The residue, boiling above 40°, amounted to 36.9 ml.

The results show that in a stream of H_2—CO mixture 2-pentene entered the reactions of hydropolymerization and hydrocondensation with CO to the extent of 13-14%, was hydrogenated to pentane to the extent of 17-18%, underwent hydrocracking to the extent of 2.5-3%, and was isomerized to 1-pentene to an insignificant extent. The residue (36 ml, b.p. >40°) was boiled over sodium (2.2 g) for six hours and then hydrogenated (33 ml) in presence of Pt/C (2.5 ml) with an addition of H_2PtCl_6; 1.6 liters of hydrogen was absorbed. The hydrogenation product (d_4^{20} 0.7130; n_D^{20} 1.4040) (23.3 ml was taken) was fractionated through a column. Table 4 gives the yields and constants of the individual fractions. The figure shows the fractionation curve of the light part (boiling up to 151°) of the hydrogenation product. The residue (9.2 ml) was fractionated from a Favorskii flask.

As can be seen from the figure and Table 4, about 52% of the hydrogenation product boiled in the range 90-150°. In tests for the presence of isoparaffins with the aid of the qualitative reaction with $FeCl_3$ [6], Fractions II, IV, V, VI, and VIII (Table 4) gave negative results, but the residue gave a positive result. The results show that the hydrogenation product consisted of C_6 and higher paraffins, mainly of normal structure with even and odd numbers of carbon atoms in their molecules.

The results show that 2-pentene, in entering into hydrocondensation with CO, is for the most part first isomerized to the 1-alkene, as in the case of 2-butene [7].

SUMMARY

1. In presence of H_2 and CO 2-pentene enters to the extent of 13-14% into reactions of hydropolymerization and hydrocondensation with CO at 190°. Simultaneously, hydrogenation to pentane occurs to the extent of 17-18% and hydrocracking to the extent of about 3%.

2. When hydrogenated, the hydrocondensate is found to consist of a mixture of saturated hydrocarbons, mainly of normal structure. This indicates that the hydrocondensation of 2-pentene with CO is largely preceded by its isomerization to 1-pentene.

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CHLOROPLATINIC ACID AS A CATALYST FOR THE ADDITION OF SILANES CONTAINING SILICON-ATTACHED HYDROGEN TO UNSATURATED COMPOUNDS

V. A. Ponomarenko, V. G. Cherkaev, A. D. Petrov, and N. A. Zadorozhnyi

In our previous communications [1-4] we have already discussed questions relating to the selection of catalysts for the addition of silanes containing silicon-attached hydrogen to olefins and have given some attention to the study of the reaction itself. A recent paper by Speier, Webster, and Barnes [5] is concerned largely with the same matters, and many of their conclusions (concerning the catalytic properties of ruthenium, the difference in the rates of addition of $HSiCl_3$ and CH_3SiHCl_2, etc.) are identical to ours. One important observation made by Speier, Webster, and Barnes is the high catalytic activity of chloroplatinic acid in the reaction under consideration, as compared with other catalysts based on Group VIII metals.

EXPERIMENTAL

In continuation of our investigation on the selection of effective catalysts for this reaction with a view to its use in the synthesis, in particular, of fluorine-containing organosilicon compounds, we also made use of chloroplatinic acid. We studied the addition of dichloromethylsilane in presence of this catalyst to the following unsaturated compounds: $CH_2 = CF_2$, $CH_2 = CH_2$, $CH \equiv CH$, $CH_2 = CH - CH_3$ and $CF_2 = CF_2$. We found that, in spite of 11 hours' heating at 160° and 50 atm in an autoclave, in presence of 10% Pt/SiO_2 CH_3SiHCl_2 added to $CH_2 = CF_2$ only to the extent of 11%,* whereas with 0.1 M $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol the yield of addition product was 34% on the dichloromethylsilane taken (43% on the amount that reacted). In the second case the pressure did not exceed 35 atm and reaction was complete in about one hour.

Under these conditions, and also in presence of 10% Pt/SiO_2, the main addition reaction

$$CH_3SiHCl_2 + CH_2 = CF_2 \rightarrow CH_3Si(Cl)_2CH_2CF_2H,$$

was accompanied by the formation of by-products: CH_3SiCl_2F, CH_3SiCl_3, $CH_3Si(Cl)_2CH_2CH_3$, and a complex mixture of telomerization products. When the reaction mixture was heated for a longer time, side reactions (probably β-breakdown reactions) leading to the formation of CH_3SiClF_2 and $CH_3Si(Cl)_2CH_2CH_3$, became more prominent. There was no change, however, in the amount of telomerization products.

In a previous investigation [4] we have already noted the screening effect of halogen atoms on the double bond (in $CF_2 = CF_2$, $CF_2 = CFCl$, and $CHCl = CCl_2$) with resulting reduced yields of addition products in presence of platinized charcoal. Since passing from $CF_2 = CF_2$ to $CF_2 = CH_2$ is accompanied by considerable increase in the yield of addition product, it would be expected that ethylene and propene, not containing fluorine atoms, would combine still more readily with CH_3SiHCl_2 in presence of H_2PtCl_6. It was in fact found that CH_3SiHCl_2 added to ethylene and to propene at room temperature at 15-20 atm in an autoclave in the course of 30 minutes.** The yields of pure $CH_3Si(Cl)_2CH_2CH_3$ and $CH_3Si(Cl)_2(CH_2)_2CH_3$ were 83% and 81.5%. The formation of telomerization products [6] was not observed. In the light of this the formation of $CH_3Si(Cl)_2CH_2CH_3$ in the addition of CH_3SiHCl_2 to $CH_2 = CF_2$ becomes understandable if β-breakdown occurs. All these considerations gave us reason to hope that CH_3SiHCl_2 would add just as readily to acetylene under these conditions. Our

* In this case 0.01% Pt/SiO_2, 0.05% Pt/SiO_2, 0.5% Pt/C and 0.5% Pd/SiO_2 did not give satisfactory results.

** Very slow addition of CH_3SiHCl_2 to ethylene was observed also at atmospheric pressure.

experiments showed that CH_3SiHCl_2 adds to acetylene with almost quantitative yield, but the rate of addition is nevertheless less than in the case of ethylene. The main experimental results and the experimental conditions are given in Table 1. The catalyst was 0.1 M $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol. Under these conditions i-$C_3H_7OH \cdot CH_3Si(Cl)_2CH_2CH_2Si(Cl)_2CH_3$ was not formed (in spite of results in [7]).

TABLE 1

Experiment No.	Unsaturated compound	Amount of CH_3SiHCl_2 (g)	Amount of catalyst (ml)	Reaction temperature (°C)	Pressure (atm); max. – min.	Reaction (hrs)	Products isolated	Amount (g)	Yield (%)
1	$CH_2 = CF_2$	124	0.25	160	35—6	2	CH_3SiCl_2F(I)	10*	
							CH_3SiHCl_2 (II)	27.5	
							$CH_3Si(Cl)_2C_2H_3$ (III)	Traces	
							$CH_3Si(Cl)_2CH_2CHF_2$ (IV)	61	34
							Telomerization products (V)	18	
2	$CH_2 = CF_2$	115	0.25	160	39—23	6	(I)	30*	
							(II)	Traces	
							(III)	6	
							(IV)	30	18
							(V)	18.3	
3	$CH_2 = CF_2$	116	0.6**	160	50—46	11	(I)	16*	
							(II)	27.5	
							(III)	Traces	
							(IV)	20	11
							(V)	7	
4	$CH_2 = CH_2$	115	0.25	20—35***	15—2	0.5	(III)	117	83****
5	$CH_3CH = CH_2$	58	0.3	20—30***	—	1	$CH_3Si(Cl)_2CH_2CH_2CH_3$ (VI)	64.5	81.5***
6	$CH \equiv CH$	64	1.2	20—25***	19—8	21	$CH_3Si(Cl)_2CH = CH_2$ (VII)	63	81****

* In ml.

** 10% Pt on SiO_2 (g).

*** Spontaneous rise of temperature.

**** Yield of crude products almost quantitative.

TABLE 2

Compound	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	MR found	MR calculated	Elementary composition (%) (found) C	H	Cl	F
(I)	28.8—29.6 (740,7)	—	—	—	—	—	—	51.75	14.82
								53.35*	14.29*
(III)**	99.5—100.2 (742)	1.0698	1.4171	—	—	24.80	5.34	50.09	—
						24.98	5.60	—	—
						25.18*	5.64*	49.57*	—
(IV)	113—113.2 (743.5)	1.2790	1.3991	34.06	34.23	20.60	3.30	39.59	21.67*
						20.52	3.28	39.18	21.54
						20.12*	3.38*	39.55*	21.22*
(VI)	124.9 (749)	—	—	—	—	—	—	—	—
(VII)	92.5 (743.2)	—	—	—	—	—	—	—	—

* Calculated from empirical formula.

** From Experiment 2 (see Table 1).

In conclusion we must point out that the main telomer obtained in the reaction of CH_3SiHCl_2 with $CF_2 = CF_2$ was $CH_3Si(Cl)_2CF_2CF_2CF_2CF_2H$. Telomerization products were formed also in the addition of CH_3SiHCl_2 to $CF_2 = CFCl$, but in this case we were unable to isolate individual compounds owing to the complex composition of the mixture of telomers. In contrast with the results of experiments with platinum supported by activated charcoal, the fractionation curve indicates that, when other carriers (SiO_2) are used, both $CH_3Si(Cl)_2CFClCFH$, and $CH_3Si(Cl)_2CF_2CFClH$, are formed.

The constants and analyses of the products are given in Table 2.

SUMMARY

1. Addition reactions of CH_3SiHCl_2 were carried out in presence of chloroplatinic acid with ethylene, propene, and acetylene at room temperature and with $CH_2 = CF_2$ and $CF_2 = CF_2$ at 160°.

2. It was shown that, as compared with reaction in presence of platinum on carriers, in the case of $CH_2 = CF_2$ the yield of addition products was increased by a factor of 3-4, whereas in the case of $CH_2 = CH_2$, $CH_2 = CH - CH_3$, and $CH \equiv CH$ almost quantitative yields were obtained.

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INVESTIGATION OF SOME OXIDATION REACTIONS OF CELLULOSE BY INFRARED SPECTROSCOPY

I. N. Ermolenko, R. G. Zhbankov, V. I. Ivanov, N. Ia. Lenshina, and V. S. Ivanova

In this paper we apply a combination of the results of chemical investigations [1] and methods of absorption spectroscopy [2] to the elucidation of the course of reactions leading to the formation of functional groups in the complex structure of the oxidation products of cellulose. It has been established previously [3] that the formation of carboxy and carbonyl groups is associated with changes in the infrared spectra. Estimates of carboxyl content [4] have been made on the basis of the absorption band at 5.57 μ associated with the C = O vibration, although this method is unreliable owing to the absorption by carbonyl groups in this region [4]. Absorption by lactone groups is displaced toward the short waves with respect to absorption by carboxyls [5]. The 6.3 μ band is characteristic for carboxylate groups. The substances examined in the present investigation were cotton cellulose and its oxidation products: monocarboxycellulose, dialdehydocellulose, and dicarboxycellulose. Their spectra were determined by means of an IKS-11 infrared spectrometer by the method that we proposed previously [6] for fibrous materials. The investigations were carried out in the absorption bands at 7 and 11 μ.

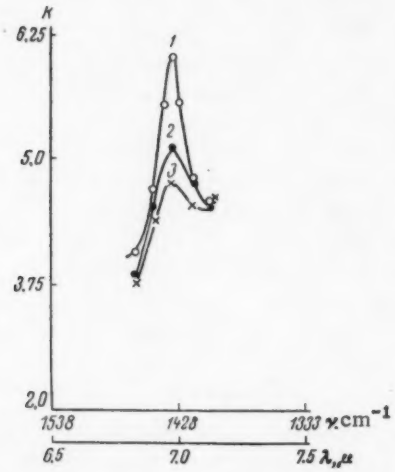

Fig. 1. Spectra of monocarboxycellulose at 7 μ: 1) unoxidized cellulose; 2) monocarboxycellulose (9.2% COOH); 3) monocarboxycellulose (16%).

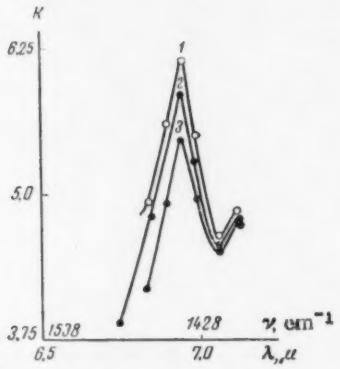

Fig. 2. Spectra of dialdehydocellulose and dicarboxycellulose at 7 μ: 1) unoxidized cellulose; 2) dialdehydocellulose (13.4% CHO); 3) dicarboxycellulose (14.7% COOH).

It is known [7] that the absorption band at 7 μ is due entirely to deformation vibrations of CH_2 groups. Hence, by the change in the intensity of absorption at this wavelength we may estimate the extent of oxidation at C-6. Monocarboxycellulose contains mainly uronic carboxyls [1, 8]. The spectra of monocarboxycelluloses

(Fig. 1, Curves 2 and 3) do indeed show a considerable reduction in the number of CH_2 groups, and this reduction is intensified by increase in the number of carboxy groups.

In the investigation of dialdehydo- and dicarboxy-celluloses on the basis of absorption at 7 μ, it was found that a reduction in the number of CH_2 groups was again observed, the reduction being greater for dicarboxycellulose (Fig. 2, Curve 3) than for dialdehydocellulose (Fig. 2, Curve 2). This indicates that under the action of $NaIO_4$ partial oxidation occurs at C-6, which is in accord with chemical data [9].

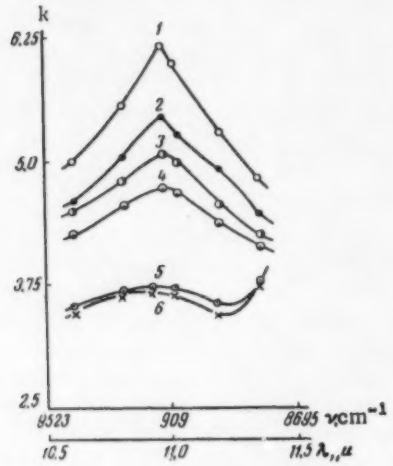

Fig. 3. Absorption spectra of oxidized celluloses at 11 μ: 1) dialdehydocellulose (13.4% CHO); dialdehydocellulose (9.2% CHO); 3) dicarboxycellulose (6.8% COOH); 4) dicarboxycellulose (12.5% COOH); 5) monocarboxycellulose (21% COOH); 6) unoxidized cellulose.

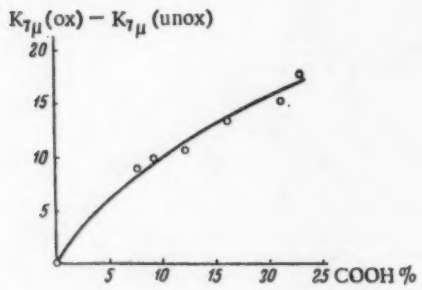

Fig. 4. Change in absorption in the region of the deformation vibration of the CH_2 group as a function of carboxyl content.

The spectra of dialdehydocelluloses have no absorption bands at 5.8 μ characteristic for the C=O group. A possible cause of this is that oxidized celluloses may contain aldehyde groups in the combined form as acetal or acylal groups [10]. We therefore investigated another method of analysis for aldehyde groups. With increase in aldehyde content, as found iodometrically, the intensity of absorption at 11 μ increased correspondingly, which is shown by comparison of the spectra of samples containing 13.4% and 9.2% of aldehyde groups (Fig. 3, Curves 1 and 2). There is a weak band at 11 μ also for unoxidized cellulose (Fig. 3, Curve 6).

The band at 11μ is not associated with carboxy groups. This follows from an examination of Fig. 3. There is no intense absorption band here in the spectrum of monocarboxycellulose (Fig. 3, Curve 5), but the spectra of dialdehydocellulose preparations that have been partially oxidized with sodium chlorite (Curves 3 and 4) have bands at 11μ of lower intensity than in the spectra of dialdehydocelluloses. Hence, in the preparations investigated aldehyde groups can be estimated in presence of carboxy groups.

We investigated also oxidation by N_2O_4 at C-6 in the repeating unit of the cellulose macromolecule as a function of the total carboxy content (Fig. 4). It will be seen from Fig. 4 that at the start of the reaction CH_2 groups disappear more rapidly than carboxy groups accumulate, though this is not so in later stages. These results indicate the accumulation of noncarboxy intermediate products at the start of the reaction.

The authors express their thanks to Professor B. I. Stepanov for valuable advice and assitance in the work.

SUMMARY

1. From the change in the intensity of the absorption band at 7μ it was established that a) oxidation of cellulose with oxides of nitrogen proceeds in its first stage with formation simultaneously of carboxy groups and noncarboxy intermediate products at C-6; b) oxidation of cellulose with sodium periodate is accompanied by partial oxidation at C-6.

2. The absorption band at 11 μ characterizes the content of aldehyde groups present in dialdehydocellulose in the combined form.

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*Original Russian pagination. See C. B. Translation.

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LETTERS TO THE EDITOR

With the object of studying the state of micro amounts of radio elements in solutions we investigated the sorption of tellurium by glass in an alkaline medium. We used the radioactive isotope Te^{127}, which has a half-life of 115 days and owing to an internal change passes into its isomer of half-life 9.3 hours (Seaborg's data). The two isomers are in radioactive equilibrium, and their life is characterized by the half-life of the parent isomer, 115 days.

In the course of the present work it was established that the fall in activity of the tellurium that separates on the glass is incomparably more rapid than the fall in the activity of tellurium in solution corresponding to the radioactive decay of Te^{127}. Activity measurements were made on the glass at definite intervals of time, and a decay curve was obtained which corresponded to the life of the Te^{127} isomer of half-life 9.3 hours. It follows from the results that under the given conditions there is selective sorption on glass of the Te^{127} isomer of half-life 9.3 hours. The explanation of this fact must be sought in the different valence states of parent and daughter Te^{127} isomers resulting from the internal conversion that occurs.

The present results give support to the method of sorption on glass as a reliable method enabling us to characterize the state of radioactive elements in solution. If similar results are obtained for isomers of other radioactive elements, the method of sorption on glass may enable us to separate isomers.

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